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VAN DER WAALS INTERACTIONS BETWEEN TWO HYDROGEN ATOMS: THE SLATER-KIRKWOOD METHOD REVISITED

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Abstract. We examine a technique of Slater and Kirkwood [22] which provides an exact resolution of the asymptotic behavior of the van der Waals attraction between two hydrogen atoms. We modify their technique to make the problem more tractable analytically and more easily solvable by numerical methods. Moreover, we prove rigorously that this approach provides an exact solution for the asymptotic electron correlation. The proof makes use of recent results [1] that utilize the Feshbach-Schur perturbation technique. We provide visual representations of the asymptotic electron correlation (entanglement) based on the use of Laguerre approximations.

Van der Waals forces play a ubiquitous role in science. The nature of the van der Waals interactions between atoms, whose attractive energy depends like $-C_6R^{-6}$ as a function of the separation distance R, has been understood for nearly a century. A mathematical argument explaining the attraction between two neutral atoms was first given by London [13], and later summarized in the book by Pauling and Wilson [17]. The interaction, known as London dispersion, is an example of quantum entanglement and cannot be rigorously explained without quantum mechanics. Work to clarify the mathematical derivation of the van der Waals interaction from many-body quantum mechanics has continued to be of interest [12, 1, 11].

In the case of two hydrogen atoms, Slater and Kirkwood [22] derived a factorization of the solution and an equation for one of the factors leading to the calculation of C_6. What is remarkable about the approach in [22] is that, in the case of two hydrogen atoms, the problem splits exactly into an angular factor and a function of two one-dimensional variables (the underlying problem is six-dimensional). Although the partial differential equation (PDE) defining the function of these two variables is not solvable in closed form, it is nevertheless easily solved by numerical techniques.

Here we provide a slightly modified version of Slater and Kirkwood's derivation in which the resulting PDE is more suitable for theoretical analysis and numerical simulation. We prove that the PDE is well posed and that, when its unique solution is multiplied by the angular factor, the resulting function solves the original six-dimensional problem. We use a Laguerre approximation to compute not only C_6 but also to display the asymptotic electron correlation visually. This simple example provides a way to see concretely the effect of electron correlation, or entanglement, that is the basis for the van der Waals effect.

We begin by recalling the heuristic approach originally used [13] to estimate the van der Waals interaction intensity. This is a perturbation argument for an eigenvalue problem. It leads to a PDE whose solution gives the asymptotic perturbation of the electron densities of the interacting atoms. It can be shown by completely different means, using recently developed techniques [1], that this equation is a valid representation. The paper is devoted to analyzing this PDE, providing numerical solutions, and justifying the perturbation method introduced by Slater and Krikwood using the Feshbach-Schur technique.

1. Interaction between two hydrogen atoms. Throughout this article, we use atomic units so that $\hbar = 1$, $e = 1$, $m_e = 1$ and $4\pi\epsilon_0 = 1$, where $\hbar$ is the reduced Planck constant, m_e the mass of the electron, e the elementary charge, and ϵ_0 the dielectric permittivity of the vacuum. In this system of units, the length unit is the Bohr (about 0.529 Ångstroms) and the energy unit is the Hartree (about 4.36×10^{-18} Joules). We consider a system of two hydrogen atoms, which, within the Born-Oppenheimer approximation, consists of two classical point-like nuclei of charge 1 and two quantum electrons of mass 1 and charge -1. We denote by R the distance separating the two nuclei, by $\mathbf{e}$ the unit vector pointing in the direction from one hydrogen atom to the other, and by $\mathbf{R}_1$ and $\mathbf{R}_2$ the positions in $\mathbb{R}^3$ of the two electrons, the origin being chosen at the center of mass of the nuclei (see Figure 1).

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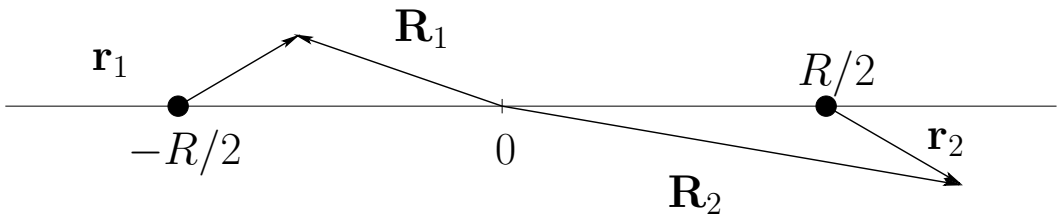

FIG. 1.1. *Coordinates for positions of nuclei and electrons in a quantum model of two hydrogen atoms.*

It is well-known that the ground state of the hydrogen molecule, which exists by virtue of Zhislin's theorem for neutral systems [26], is a singlet spin state [9]

$$\Psi_R(\mathbf{R}_1,\mathbf{R}_2)\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}}, \tag{1.1}$$

where the spatial component Ψ_R of the ground state is symmetric ($\Psi_R(\mathbf{R}_1,\mathbf{R}_2) = \Psi_R(\mathbf{R}_2,\mathbf{R}_1)$). Moreover, Ψ_R can be characterized as the nondegenerate lowest eigenstate of the spin-less Schrödinger equation applied to real functions without symmetry, that is, the minimum energy over all functions corresponds to a symmetric eigenfunction. Thus $\Psi_R(\mathbf{R}_1,\mathbf{R}_2)$ satisfies the normalization constraint

$$\int_{\mathbb{R}^3\times\mathbb{R}^3} |\Psi_R(\mathbf{R}_1,\mathbf{R}_2)|^2\, d\mathbf{R}_1\, d\mathbf{R}_2 = 1,$$

and the six-dimensional Schrödinger equation

$$-\frac{1}{2}\Delta_{\mathbf{R}_1}\Psi_R(\mathbf{R}_1,\mathbf{R}_2) - \frac{1}{2}\Delta_{\mathbf{R}_2}\Psi_R(\mathbf{R}_1,\mathbf{R}_2) + W_R(\mathbf{R}_1,\mathbf{R}_2)\Psi_R(\mathbf{R}_1,\mathbf{R}_2) = E_R\Psi_R(\mathbf{R}_1,\mathbf{R}_2), \tag{1.2}$$

where $\Delta_{\mathbf{R}_k}$ is the Laplace operator with respect to the variables $\mathbf{R}_k \in \mathbb{R}^3$, where

$$W_R(\mathbf{R}_1,\mathbf{R}_2) = -\frac{1}{|\mathbf{R}_1 - \frac{1}{2}R\mathbf{e}|} - \frac{1}{|\mathbf{R}_2 - \frac{1}{2}R\mathbf{e}|} - \frac{1}{|\mathbf{R}_1 + \frac{1}{2}R\mathbf{e}|} - \frac{1}{|\mathbf{R}_2 + \frac{1}{2}R\mathbf{e}|} + \frac{1}{|\mathbf{R}_1 - \mathbf{R}_2|} + \frac{1}{R}, \tag{1.3}$$

and where E_R is the lowest eigenvalue of the self-adjoint operator $-\frac{1}{2}\Delta_{\mathbf{R}_1} - \frac{1}{2}\Delta_{\mathbf{R}_2} + W_R$ on $L^2(\mathbb{R}^3\times\mathbb{R}^3)$. The proof of uniqueness of the ground state, and thus its positivity and symmetry, can be achieved by a standard argument using Harnack's inequality [7] on the complement of the singularity set of W_R which is of co-dimension 3. The interaction energy between the two atoms is given by

$$\delta E(R) = E_R - E_\infty = E_R + 1,$$

as in the limit $R = +\infty$ the two hydrogen atoms do not interact and the energy of the system is then twice the energy of a single hydrogen atom, that is $E_\infty = 2\times(-1/2) = -1$.

In order to study the asymptotic limit when R goes to infinity, it is convenient to make the following changes of variable

$$\mathbf{R}_1 = -R/2\mathbf{e} + \mathbf{r}_1, \quad \mathbf{R}_2 = R/2\mathbf{e} + \mathbf{r}_2, \quad R = \epsilon^{-1/3},$$

$$\psi_\epsilon(\mathbf{r}_1,\mathbf{r}_2) = \Psi_{\epsilon^{-1/3}}\big(-\tfrac{1}{2}\epsilon^{-1/3}\mathbf{e} + \mathbf{r}_1, \tfrac{1}{2}\epsilon^{-1/3}\mathbf{e} + \mathbf{r}_2\big), \quad \lambda_\epsilon = E_{\epsilon^{-1/3}}.$$

Denoting respectively by $(\cdot,\cdot)$ and $\|\cdot\|$ the scalar product and the norm of $L^2(\mathbb{R}^6)$, the function $\psi_\epsilon(\mathbf{r}_1,\mathbf{r}_2)$ satisfies, for all $\epsilon > 0$, the normalization condition $\|\psi_\epsilon\| = 1$ and is the ground state of the Schrödinger equation

$$(H_0 + V_\epsilon)\psi_\epsilon = \lambda_\epsilon\psi_\epsilon, \tag{1.4}$$

where

$$H_0 = -\frac{1}{2}\Delta_{\mathbf{r}_1} - \frac{1}{|\mathbf{r}_1|} - \frac{1}{2}\Delta_{\mathbf{r}_2} - \frac{1}{|\mathbf{r}_2|} \tag{1.5}$$

and where the correlation potential V_ϵ satisfies

$$V_\epsilon(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{|\mathbf{r}_1 - \epsilon^{-1/3}\mathbf{e}|} - \frac{1}{|\mathbf{r}_2 + \epsilon^{-1/3}\mathbf{e}|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2 - \epsilon^{-1/3}\mathbf{e}|} + \epsilon^{1/3}. \tag{1.6}$$

Recall that the normalized ground state (λ_0, ψ_0) of the Hamiltonian H_0 is known explicitly:

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \pi^{-1} e^{-(|\mathbf{r}_1| + |\mathbf{r}_2|)}, \quad \lambda_0 = -1. \tag{1.7}$$

The interaction energy of the two hydrogen atoms is therefore given by

$$\delta E(R) = \lambda_{R^{-3}} - \lambda_0,$$

and can be computed to high accuracy [25] as shown in Figure 3.1. Similar data can be found in [10].

2. Van der Waals interaction. To understand the asymptotic behavior of the interaction energy $\delta E(R) = \lambda_{R^{-3}} - \lambda_0$ for large R, we need to understand the asymptotic behavior of λ_ϵ for ϵ small. Two classical methods can be used to estimate this quantity, namely the Rayleigh-Ritz method and the perturbation method.

2.1. Rayleigh-Ritz variational method. The energy λ_ϵ can be bounded above by the Rayleigh-Ritz variational method as

$$\lambda_\epsilon = \min_{\psi \in X \setminus \{0\}} \mathcal{R}_\epsilon(\psi), \quad \mathcal{R}_\epsilon(\psi) := \frac{(\psi, (H_0 + V_\epsilon)\psi)}{\|\psi\|^2}. \tag{2.1}$$

An upper bound of λ_ϵ is obtained by minimizing the Rayleigh quotient $\mathcal{R}_\epsilon(\psi)$ over a subset of $X \setminus \{0\}$, where the function space X is the form domain of the operator H_0 ($X = H^1(\mathbb{R}^6)$ in the case of two hydrogen atoms).

It was thus possible for London [17] to approximate the interaction energy for two hydrogen atoms to a remarkable degree of accuracy using (2.1). It was found that

$$\lambda_\epsilon - \lambda_0 \leq -C_6\epsilon^2 = -C_6 R^{-6}, \tag{2.2}$$

where R is the separation distance ($\epsilon = R^{-3}$). Subsequent studies [15, 16] have carried out similar computations to estimate C_6 for hydrogen and other atoms to high accuracy by similar methods. Recently, a rigorous derivation of the expression for C_6 for general atomic interactions has been given [1].

Lieb and Thirring [12] were able to show that the R^{-6} upper bound was rigorously valid for a wide range of molecular interactions. They used the Rayleigh-Ritz formula (2.1) with a special choice of trial functions.

2.2. Perturbation method. Formally in this case,

$$V_\epsilon = \epsilon\mathcal{B} + o(\epsilon), \tag{2.3}$$

where $\mathcal{B}$ is a symmetric multiplication operator defined subsequently in (3.2). The first-order perturbation theory for such an eigenproblem seeks

$$\begin{aligned} \psi_\epsilon &= \psi_0 + \epsilon\psi' + o(\epsilon) \\ \lambda_\epsilon &= \lambda_0 + \epsilon\lambda' + o(\epsilon), \end{aligned} \tag{2.4}$$

where

$$\begin{aligned} H_0\psi_0 &= \lambda_0\psi_0 \\ \|\psi_0\| &= 1 \end{aligned} \tag{2.5}$$

and

$$\begin{aligned}(H_0-\lambda_0)\psi' &= \lambda'\psi_0 - \mathcal{B}\psi_0\\ (\psi',\psi_0) &= 0.\end{aligned} \tag{2.6}$$

Since ψ_0 depends only on radial variables, we will see that $(\psi_0,\mathcal{B}\psi_0)=0$. From this we get, using (2.5) and the self-adjointness of H_0,

$$\lambda' = (\psi_0,\mathcal{B}\psi_0) + (\psi_0,(H_0-\lambda_0)\psi') = 0. \tag{2.7}$$

To obtain the leading term of the interaction energy, we therefore need to carry out the perturbation to higher order, as observed in [17]. Since V_ϵ is (formally) analytic in $R^{-1}=\epsilon^{1/3}$, i.e., $V_\epsilon = \epsilon\mathcal{B}+\epsilon^{4/3}\mathcal{C}+\cdots$, we make the ansatz

$$\psi_\epsilon = \psi_0 + \sum_{i=3}^{6}\epsilon^{i/3}\psi^{(i)} + o(\epsilon^2), \tag{2.8}$$

where we have temporarily written $\psi'=\psi^{(3)}$. Since $\|\psi_\epsilon\|_{L^2(\mathbb{R}^6)} = \|\psi_0\|_{L^2(\mathbb{R}^6)} = 1$, we see that

$$\begin{aligned}0 &= 2\Big(\psi_0,\sum_{i=3}^{6}\epsilon^{i/3}\psi^{(i)}\Big) + \Big(\sum_{i=3}^{6}\epsilon^{i/3}\psi^{(i)},\sum_{i=3}^{6}\epsilon^{i/3}\psi^{(i)}\Big) + o(\epsilon^2)\\ &= 2\Big(\psi_0,\sum_{i=4}^{6}\epsilon^{i/3}\psi^{(i)}\Big) + \epsilon^2\big(\psi^{(3)},\psi^{(3)}\big) + o(\epsilon^2)\\ &= 2\Big(\psi_0,\sum_{i=4}^{5}\epsilon^{i/3}\psi^{(i)}\Big) + \epsilon^2\Big(2\big(\psi_0,\psi^{(6)}\big) + \big(\psi^{(3)},\psi^{(3)}\big)\Big) + o(\epsilon^2).\end{aligned} \tag{2.9}$$

Dividing (2.9) by $\epsilon^{4/3}$, and letting $\epsilon\to 0$, we conclude that $(\psi_0,\psi^{(4)})=0$. Next, dividing (2.9) by $\epsilon^{5/3}$, and letting $\epsilon\to 0$, we conclude that $(\psi_0,\psi^{(5)})=0$. Therefore $(\psi^{(i)},H_0\psi_0)=\lambda_0(\psi^{(i)},\psi_0)=0$ as well for $i=3,4,5$. Finally, dividing (2.9) by ϵ^2 and letting $\epsilon\to 0$, we conclude that

$$2\big(\psi_0,\psi^{(6)}\big) + \big(\psi^{(3)},\psi^{(3)}\big) = 0. \tag{2.10}$$

Expanding again, we have

$$\begin{aligned}(\psi_\epsilon,H_0\psi_\epsilon) =&(\psi_0,H_0\psi_0) + 2\Big(\psi_0,\sum_{i=3}^{6}\epsilon^{i/3}H_0\psi^{(i)}\Big) + \Big(\sum_{i=3}^{6}\epsilon^{i/3}\psi^{(i)},\sum_{i=3}^{6}\epsilon^{i/3}H_0\psi^{(i)}\Big) + o\left(\epsilon^2\right)\\ =&\lambda_0 + 2\lambda_0\Big(\psi_0,\sum_{i=3}^{6}\epsilon^{i/3}\psi^{(i)}\Big) + \Big(\sum_{i=3}^{6}\epsilon^{i/3}\psi^{(i)},\sum_{i=3}^{6}\epsilon^{i/3}H_0\psi^{(i)}\Big) + o\left(\epsilon^2\right)\\ =&\lambda_0 + 2\lambda_0\epsilon^2\big(\psi_0,\psi^{(6)}\big) + \epsilon^2\big(\psi^{(3)},H_0\psi^{(3)}\big) + o\left(\epsilon^2\right)\\ =&\lambda_0 - \lambda_0\epsilon^2\big(\psi^{(3)},\psi^{(3)}\big) + \epsilon^2\big(\psi^{(3)},H_0\psi^{(3)}\big) + o\left(\epsilon^2\right)\end{aligned} \tag{2.11}$$

in view of (2.10). Also note that

$$(\psi_\epsilon,V_\epsilon\psi_\epsilon) = (\psi_0,V_\epsilon\psi_0) + 2\epsilon^2(\psi^{(3)},\mathcal{B}\psi_0) + o\left(\epsilon^2\right). \tag{2.12}$$

Putting together (2.11) and (2.12) we find

$$\begin{aligned}\lambda_\epsilon =&(\psi_\epsilon,(H_0+V_\epsilon)\psi_\epsilon) = (\psi_\epsilon,H_0\psi_\epsilon) + (\psi_\epsilon,V_\epsilon\psi_\epsilon)\\ =&\lambda_0 + \epsilon^2\big(\psi^{(3)},(H_0-\lambda_0)\psi^{(3)} + 2\mathcal{B}\psi_0\big) + (\psi_0,V_\epsilon\psi_0) + o\left(\epsilon^2\right)\\ =&\lambda_0 + \epsilon^2\big(\psi^{(3)},\mathcal{B}\psi_0\big) + (\psi_0,V_\epsilon\psi_0) + o\left(\epsilon^2\right),\end{aligned} \tag{2.13}$$

where we used (2.6) at the last step (recall $\psi' = \psi^{(3)}$). The quantity

$$\nu_\epsilon = (\psi_0, V_\epsilon \psi_0) = e^{-2R}\left(\frac{1}{R} + \frac{5}{8} - \frac{3R}{4} - \frac{R^2}{6}\right) \quad (R^{-3} = \epsilon) \tag{2.14}$$

has been known for some time [23, 2]. Thus

$$\lambda_\epsilon - \lambda_0 = \epsilon^2(\psi', \mathcal{B}\psi_0) + o\left(\epsilon^2\right).$$

where we have switched back to the notation $\psi' = \psi^{(3)}$. We therefore have

$$\delta E(R) = -\frac{C_6}{R^6} + o(R^{-6}), \tag{2.15}$$

where

$$C_6 = -(\psi', \mathcal{B}\psi_0) = ((H_0 - \lambda_0)\psi', \psi'). \tag{2.16}$$

The first order perturbation ψ' allows one to compute explicitly the coefficient C_6. This function is also interesting in itself since it represents the asymptotic electron correlation.

The above derivation of the expression of C_6 is still heuristic in the sense that we have not proved that the expansions in ϵ are rigorously valid. The mathematical difficulty arises from the fact that the perturbation V_ϵ does not tend to zero as a multiplication operator from $D(H_0) = H^2(\mathbb{R}^6)$ to $L^2(\mathbb{R}^6)$, so that regular perturbation theory [19, Section XII.2] does not apply. However, with a different approach known as the Feshbach-Schur perturbation method [8], it is proved in Section 5, using the ideas of [1], that the equalities (2.15) and (2.16), with ψ' given by (2.6), hold true. In Section 5, we also verify that

$$\|\psi_\epsilon - \psi_0 - \epsilon\psi'\|_{H^2(\mathbb{R}^6)} = \mathrm{o}(\epsilon).$$

To do so, we need some regularity and decay properties of ψ' that we derive based on the structure of the equation (2.6) in the case of two hydrogen atoms. Thus we take the problem (2.6) as our starting point, and we will derive rigorously results about the equation and its solution.

2.3. Computing C_6. In view of the previous two sections, we can imagine two different approaches to computing C_6. Thus we can compute the limit of the functionals or a functional of the limit:

$$\begin{array}{ccc} \epsilon^{-1}(\mathrm{PDE}_\epsilon - \mathrm{PDE}_0) & \xrightarrow{\text{Rayleigh-Ritz method}} & (\lambda_\epsilon - \lambda_0)/\epsilon^2 \\ \Big\downarrow{\scriptstyle \epsilon\to 0} & & \Big\downarrow{\scriptstyle \epsilon\to 0} \\ \text{limiting PDE} & \xrightarrow{\text{functional of } \psi'} & -C_6\,. \end{array} \tag{2.17}$$

The approach using the Rayleigh-Ritz method (2.1) consists in approximating $\lambda_\epsilon - \lambda_0$ (recall that $\epsilon = R^{-3}$) and computing its limit, using the upper right side of (2.17).

The main strategy for using (2.1) is to pick $\psi = \psi_0 + w$ where $w \in \psi_0^\perp$, since directions proportional to ψ_0 do not add anything. Here and in the sequel, we use the notation

$$\psi_0^\perp = \left\{ f \in L^2(\mathbb{R}^6) \,:\, (f, \psi_0) = 0 \right\}. \tag{2.18}$$

In physical terms, there is a basis set of functions for the set of functions $w \perp \psi_0$, and this basis consists of the excited states of the atoms (including diffusion states corresponding to the continuous spectrum). For this reason, there has been some confusion in the literature about van der Waals forces being related to excited states. Quite the contrary, the best choice in (2.1) is $\psi = \psi_0 + \epsilon\psi'$ where ψ' encodes the asymptotic form of the electron correlation. Although it can be expanded as a sum of excited states, the physical interpretation is quite different.

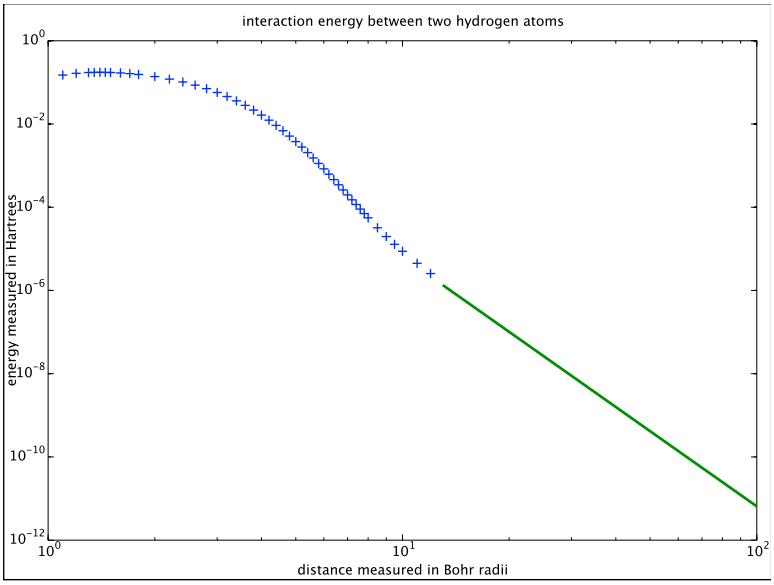

FIG. 3.1. *Interaction energy (van der Waals energy) between two hydrogen atoms. The unit for the vertical scale is the Hartree, and the unit for the horizontal scale is the Bohr. Distinct points are the data in Table II in [25], and the solid line corresponds to the asymptotic expression* C_6R^{-6} *with* $C_6 = 6.4990267$ *[4]. The breakpoint between the data and the asymptotic model corresponds to* $R \approx 10 Bohr \approx 5 \mathring{A}$*, or* $\epsilon \approx 0.0005$.

3. Slater-Kirkwood approach. Here we propose to use instead the lower left side of (2.17) to first compute the limiting equation, and then express C_6 in terms of its solution. We have seen that the Rayleigh-Ritz approach is limited since the derivative λ' of λ_ϵ with respect to ϵ vanishes at $\epsilon = 0$, causing this approach to be a second-order perturbation. On the other hand, the limiting PDE does have a nonzero solution, so the first-order perturbation related to the wave function does not vanish.

It is well known (e.g., [5]) that the correlation potential V_ϵ satisfies

$$V_\epsilon(\mathbf{r}_1, \mathbf{r}_2) = \epsilon\big(\mathbf{r}_1 \cdot \mathbf{r}_2 - 3\,(\mathbf{r}_1 \cdot \mathbf{e})\,(\mathbf{r}_2 \cdot \mathbf{e})\,\big) + \mathcal{O}\big(\epsilon^{4/3}\big). \tag{3.1}$$

Thus the interaction of two hydrogen atoms corresponds to the model in Section 2.2 with

$$\mathcal{B}(\mathbf{r}_1, \mathbf{r}_2) = \mathbf{r}_1 \cdot \mathbf{r}_2 - 3\,(\mathbf{r}_1 \cdot \mathbf{e})\,(\mathbf{r}_2 \cdot \mathbf{e})\,. \tag{3.2}$$

The expression $\epsilon\mathcal{B}$ is the asymptotic dipole-dipole interaction potential for two dipoles placed a distance $R = \epsilon^{-1/3}$ apart along a vector $\mathbf{e}$ [5]. The approximation (3.1) can be made precise via

$$\sup_{|\mathbf{r}_1|+|\mathbf{r}_2|\leq K} |V_\epsilon(\mathbf{r}_1, \mathbf{r}_2) - \epsilon\mathcal{B}(\mathbf{r}_1, \mathbf{r}_2)| \leq CK^3\epsilon^{4/3}. \tag{3.3}$$

We therefore need to solve

$$\boxed{(H_0 - \lambda_0)\psi' = -\mathcal{B}\psi_0, \quad (\psi_0, \psi') = 0,} \tag{3.4}$$

where H_0, ψ_0, λ_0 and $\mathcal{B}$ are given in (1.5), (1.7), and (3.2). Equation (3.4) is the analog of (2.6) in the case of two interacting hydrogen atoms. This is still a PDE in six dimensions, so it is of significant interest that this can be factored, as observed by Slater and Kirkwood [22].

3.1. Separation of variables. Let us attempt to represent the solution to (3.4) as

$$\psi'(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{B}(\mathbf{r}_1, \mathbf{r}_2)S(|\mathbf{r}_1|, |\mathbf{r}_2|). \tag{3.5}$$

The function S is closely related to the function R in [22]. Define

$$\Omega = \left\{(r_1, r_2) \in \mathbb{R}^2 \,:\, r_i > 0\right\}. \tag{3.6}$$

In addition to $S : \Omega \to \mathbb{R}$, define $\widetilde{S} : \mathbb{R}^6 \to \mathbb{R}$ by $\widetilde{S}(\mathbf{r}_1, \mathbf{r}_2) = S(|\mathbf{r}_1|, |\mathbf{r}_2|)$. We have

$$\Delta(\mathcal{B}\widetilde{S}) = \mathcal{B}\Delta\widetilde{S} + 2\nabla\mathcal{B} \cdot \nabla\widetilde{S} \tag{3.7}$$

since $\Delta\mathcal{B} = 0$. Then

$$\nabla\mathcal{B}(\mathbf{r}_1, \mathbf{r}_2) = (\mathbf{r}_2 - 3\mathbf{e}(\mathbf{r}_2 \cdot \mathbf{e}), \mathbf{r}_1 - 3\mathbf{e}(\mathbf{r}_1 \cdot \mathbf{e})) \tag{3.8}$$

and

$$\nabla\widetilde{S}(\mathbf{r}_1, \mathbf{r}_2) = ((S_{,1}/|\mathbf{r}_1|)\mathbf{r}_1, (S_{,2}/|\mathbf{r}_2|)\mathbf{r}_2), \tag{3.9}$$

where $S_{,i} = \partial S/\partial r_i$. Note that

$$\mathbf{r}_1 \cdot (\mathbf{r}_2 - 3e(\mathbf{r}_2 \cdot \mathbf{e})) = \mathcal{B}(\mathbf{r}_1, \mathbf{r}_2) \;\text{ and }\; \mathbf{r}_2 \cdot (\mathbf{r}_1 - 3e(\mathbf{r}_1 \cdot \mathbf{e})) = \mathcal{B}(\mathbf{r}_1, \mathbf{r}_2). \tag{3.10}$$

Thus $(a\mathbf{r}_1, b\mathbf{r}_2) \cdot \nabla\mathcal{B}(\mathbf{r}_1, \mathbf{r}_2) = (a + b)\mathcal{B}(\mathbf{r}_1, \mathbf{r}_2)$, and

$$\nabla\mathcal{B}(\mathbf{r}_1, \mathbf{r}_2) \cdot \nabla\widetilde{S}(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{B}(\mathbf{r}_1, \mathbf{r}_2)\Big(\frac{S_{,1}}{|\mathbf{r}_1|} + \frac{S_{,2}}{|\mathbf{r}_2|}\Big). \tag{3.11}$$

Therefore

$$\Delta(\mathcal{B}\widetilde{S}) = \mathcal{B}\left(\Delta\widetilde{S} + 2\Big(\frac{S_{,1}}{|\mathbf{r}_1|} + \frac{S_{,2}}{|\mathbf{r}_2|}\Big)\right). \tag{3.12}$$

Thus

$$(H_0 - \lambda_0)(\mathcal{B}\widetilde{S}) = \mathcal{B}\left((H_0 - \lambda_0)\widetilde{S} - \frac{S_{,1}}{|\mathbf{r}_1|} - \frac{S_{,2}}{|\mathbf{r}_2|}\right). \tag{3.13}$$

So if S satisfies

$$(H_0 - \lambda_0)\widetilde{S} - \frac{S_{,1}}{|\mathbf{r}_1|} - \frac{S_{,2}}{|\mathbf{r}_2|} = -\psi_0, \tag{3.14}$$

then $\psi' = \mathcal{B}\widetilde{S}$ satisfies (3.4). Note that $\psi' = \mathcal{B}\widetilde{S} \perp \psi_0$ if $\widetilde{S} \perp \mathcal{B}\psi_0$.

If we write $\mathbf{r}_1 = |\mathbf{r}_1|\mathbf{s}_1$ and $\mathbf{r}_2 = |\mathbf{r}_2|\mathbf{s}_2$, we can separate variables in $\mathcal{B}$ as

$$\mathcal{B}(\mathbf{r}_1, \mathbf{r}_2) = |\mathbf{r}_1|\,|\mathbf{r}_2|\,(\mathbf{s}_1 \cdot \mathbf{s}_2 - 3\,(\mathbf{s}_1 \cdot \mathbf{e})\,(\mathbf{s}_2 \cdot \mathbf{e})) = |\mathbf{r}_1|\,|\mathbf{r}_2|\,b(\mathbf{s}_1, \mathbf{s}_2), \tag{3.15}$$

where the variables $\mathbf{s}_i$ are on the 2-sphere $\mathbb{S}_2$. Here b is defined on $(\mathbb{S}_2)^2$ by

$$b(\mathbf{s}_1, \mathbf{s}_2) = \mathbf{s}_1 \cdot \mathbf{s}_2 - 3\,(\mathbf{s}_1 \cdot \mathbf{e})\,(\mathbf{s}_2 \cdot \mathbf{e})\,. \tag{3.16}$$

The condition $\widetilde{S} \perp \mathcal{B}\psi_0$ is automatically satisfied since,

$$\int_{\mathbb{R}^6} \widetilde{S}\mathcal{B}\psi_0\, d\mathbf{r}_1 d\mathbf{r}_2 = \int_{\mathbb{S}_2}\int_{\mathbb{S}_2} b(\mathbf{s}_1, \mathbf{s}_2)\, d\mathbf{s}_1 d\mathbf{s}_2 \int_0^\infty \int_0^\infty S(r_1, r_2)\hat{\psi}_0(r_1, r_2)\, dr_1 dr_2 = 0, \tag{3.17}$$

since the angular integral vanishes, where $\hat{\psi}_0(|\mathbf{r}_1|, |\mathbf{r}_2|) = \psi_0(\mathbf{r}_1, \mathbf{r}_2)$, that is, $\hat{\psi}_0(r_1, r_2) = \frac{1}{\pi}e^{-(r_1+r_2)}$.

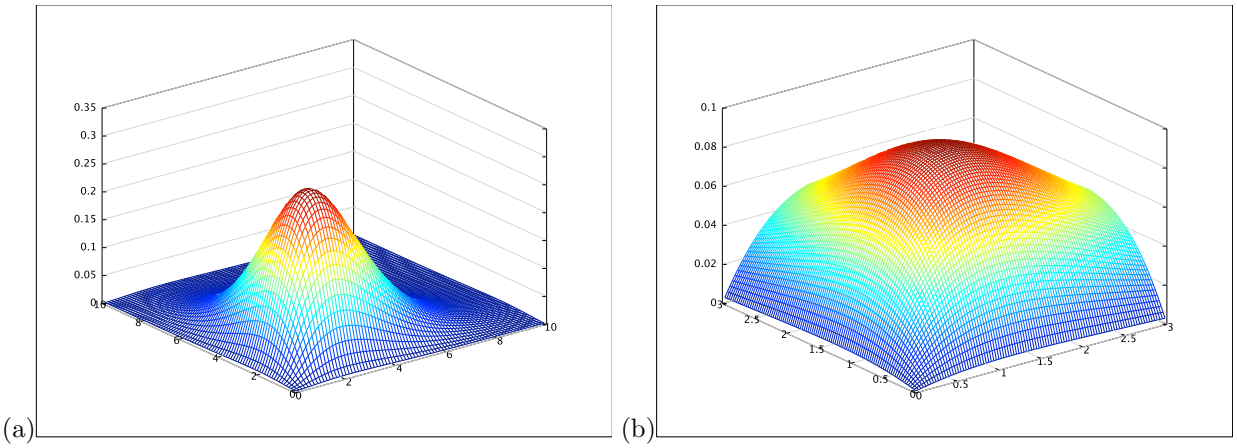

FIG. 3.2. *Plots of (a) $-T(r_1,r_2)$ and (b) $-T(r_1,r_2)/(r_1r_2) = -\psi'(r_1\mathbf{s}_1, r_2\mathbf{s}_2)/b(\mathbf{s}_1,\mathbf{s}_2)$, where T is the unique solution in $H^1_0(\Omega)$ of the equation (3.24), b is defined in* (3.16)*, and ψ' is defined in* (3.28)*. The vertical scale has been chosen so that the amplitude (maximum) of the ground state wave function ψ_0 is one instead of the actual value of $1/\pi$ to make the comparison easier between ψ_0 and the perturbation $\epsilon\psi'$. The unit for the two horizontal axes r_1 and r_2 is the Bohr. Computational details are given in Section 3.4. The degree of Laguerre functions used was $k = 9$.*

Using spherical coordinates, we can write

$$H_0\widetilde{S} = -\frac{1}{2}\left(S_{,11} + S_{,22}\right) - \frac{S_{,1}}{|\mathbf{r}_1|} - \frac{S_{,2}}{|\mathbf{r}_2|} - \frac{S}{|\mathbf{r}_1|} - \frac{S}{|\mathbf{r}_2|}. \tag{3.18}$$

Therefore (3.13) becomes

$$-\frac{1}{2}\left(S_{,11} + S_{,22}\right) - 2\left(\frac{S_{,1}}{r_1} + \frac{S_{,2}}{r_2}\right) - \left(\frac{1}{r_1} + \frac{1}{r_2}\right)S - \lambda_0 S = -\hat{\psi}_0. \tag{3.19}$$

Similarly, from (2.16) and (3.5), we have

$$\begin{aligned} C_6 &= -(\psi_0, \mathcal{B}\psi') = -(\psi_0, \mathcal{B}^2\widetilde{S}) \\ &= -\int_{\mathbb{S}_2}\int_{\mathbb{S}_2} b(\mathbf{s}_1,\mathbf{s}_2)^2\, d\mathbf{s}_1 d\mathbf{s}_2 \int_0^\infty\int_0^\infty \hat{\psi}_0(r_1,r_2) r_1^4 r_2^4 S(r_1,r_2)\, dr_1 dr_2, \end{aligned} \tag{3.20}$$

where the extra factor $r_1^2 r_2^2$ comes from the Jacobian in the transformation to spherical coordinates. The angular integral can be computed analytically:

$$\int_{\mathbb{S}_2}\int_{\mathbb{S}_2} b(\mathbf{s}_1,\mathbf{s}_2)^2\, d\mathbf{s}_1 d\mathbf{s}_2 = \frac{32\pi^2}{3}. \tag{3.21}$$

This calculation is detailed in Section 3.5.

3.2. Understanding S. Our numerical simulations suggest that S does not vanish at the boundary of Ω. It is therefore not obvious how to make sense of the equation (3.19) due to the singularities. In order to circumvent these difficulties and to obtain a symmetric equation, we consider the function

$$T(r_1,r_2) = (r_1r_2)^2 S(r_1,r_2). \tag{3.22}$$

Let us see what sort of equation T satisfies. We compute the Laplacian of the product and use (3.19) to simplify its expression:

$$\begin{aligned}\Delta_2 T &= (r_1 r_2)^2 \Delta_2 S + 4 r_1 r_2 (r_2, r_1)\cdot \nabla S + 2(r_1^2 + r_2^2) S \\ &= (r_1 r_2)^2 \left(\Delta_2 S + 4\left(\frac{S_{,1}}{r_1} + \frac{S_{,2}}{r_2} \right) + 2\left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) S \right) \\ &= -2\left(\frac{1}{r_1} + \frac{1}{r_2} \right) T - 2\lambda_0 T + 2(r_1 r_2)^2 \hat{\psi}_0 + 2\left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) T,\end{aligned} \tag{3.23}$$

where here $\Delta_2 w = w_{,11} + w_{,22}$. Therefore T solves the equation

$$\boxed{-\frac{1}{2}\Delta_2 T(r_1, r_2) + (\kappa(r_1) + \kappa(r_2))\, T(r_1, r_2) = -(r_1 r_2)^2 \hat{\psi}_0(r_1, r_2),} \tag{3.24}$$

where the function κ is defined by

$$\kappa(r) = r^{-2} - r^{-1} - \tfrac{1}{2}\lambda_0 = r^{-2} - r^{-1} + \tfrac{1}{2}. \tag{3.25}$$

The minimum of κ occurs at $r = 2$, and we have $\kappa(r) \geq \frac{1}{4}$. This problem is well posed in $H_0^1(\Omega)$, i.e., given Dirichlet conditions on the boundary of the quarter-plane Ω defined in (3.6), as we demonstrate in Section 3.3. From (3.20) and (3.21),

$$\boxed{C_6 = -\frac{32}{3}\pi \int_0^\infty \int_0^\infty r_1^2 r_2^2 e^{-(r_1 + r_2)} T(r_1, r_2)\, dr_1 dr_2.} \tag{3.26}$$

The solution for T in (3.24) is depicted in Figure 3.2, and in Table 3.1 we see values of C_6, both computed using Laguerre function approximation (cf. Section 3.4).

Recall from (3.5) that

$$\psi'(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{B}(\mathbf{r}_1, \mathbf{r}_2) S(|\mathbf{r}_1|, |\mathbf{r}_2|) = \mathcal{B}(\mathbf{r}_1, \mathbf{r}_2) \frac{T(|\mathbf{r}_1|, |\mathbf{r}_2|)}{|\mathbf{r}_1|^2 |\mathbf{r}_2|^2}, \tag{3.27}$$

so that

$$\psi'(\mathbf{r}_1, \mathbf{r}_2) = b(|\mathbf{r}_1|^{-1}\mathbf{r}_1, |\mathbf{r}_2|^{-1}\mathbf{r}_2) \frac{T(|\mathbf{r}_1|, |\mathbf{r}_2|)}{|\mathbf{r}_1|\, |\mathbf{r}_2|}, \tag{3.28}$$

where $b(\mathbf{s}_1, \mathbf{s}_2)$ is defined in (3.16).

THEOREM 3.1. *The function ψ' defined in* (3.28)*, where b is defined in* (3.16) *and T is the unique solution in $H_0^1(\Omega)$ of* (3.24)*, belongs to $H^2(\mathbb{R}^6)$ and is the unique solution of* (3.4) *in $L^2(\mathbb{R}^6)$. Moreover, ψ' decays exponentially at infinity.*

In Figure 3.3, we see a comparison of the spatial factor T of the perturbation ψ' with the ground-state wave function $\hat{\psi}_0$ along the diagonal (r, r) in (r_1, r_2) coordinates. The minimum of $\psi'(r\mathbf{s}_1, r\mathbf{s}_2)/b(\mathbf{s}_1, \mathbf{s}_2) = T(r, r)/r^2$ occurs near 1.3 Bohr, and the minimum value is just less than -0.092 of the amplitude (maximum) of ψ_0, that is, less than 10%. At that point, $\psi_0 \approx 0.076$ of the amplitude of ψ_0, but it should be remembered that, according to Figure 3.1, the asymptotic model fails to provide accurate approximations of the interaction energy for ϵ much bigger than 0.0005, or for R smaller than about 10 Bohr $\approx$ 5Å. Thus $\epsilon\psi'$ represents a relatively small perturbation to ψ_0 in the range of ϵ values of interest.

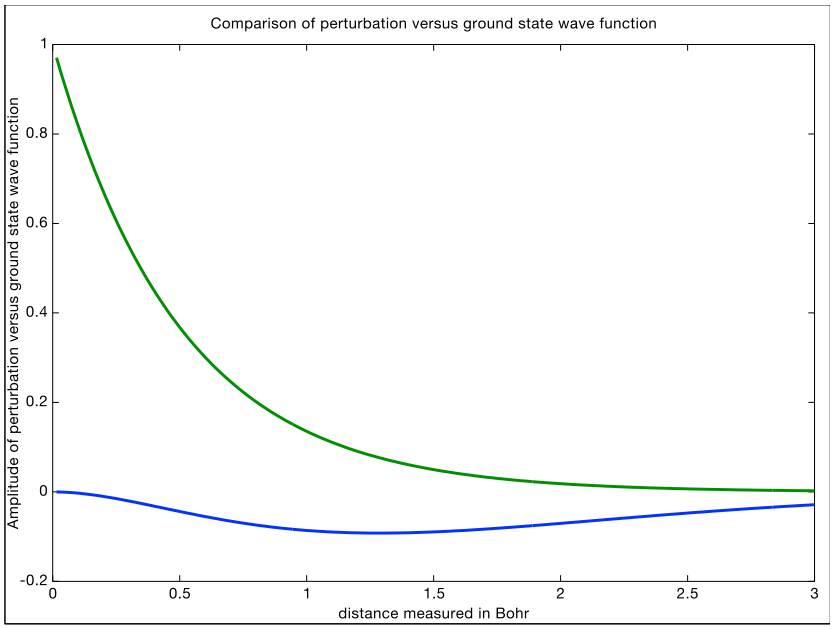

FIG. 3.3. *Comparison of perturbation* $\psi'(r\mathbf{s}_1, r\mathbf{s}_2)/b(\mathbf{s}_1, \mathbf{s}_2)$ *(lower curve) with ground-state wave function* $\psi_0(r\mathbf{s}_1, r\mathbf{s}_2)$ *(upper curve). The vertical scale has been chosen so that the amplitude of the ground state wave function is one instead of the actual value of* $1/\pi$ *to make the comparison easier between* ψ_0 *and the perturbation. The unit for the horizontal scale is the Bohr.*

3.3. Well posedness of equation (3.24)**.** Recall the definition of $\Omega = (0,\infty)^2$ from (3.6). We want to prove the following.

LEMMA 3.2. *The PDE* (3.24) *has a unique solution* T *in* $H^1_0(\Omega)$ *which decays exponentially at infinity. More precisely, for any* $\alpha < \frac{1}{2}\sqrt{3}$*, there is a constant* $C_\alpha < \infty$ *such that* $\|T(\mathbf{r})e^{\alpha(r_1+r_2)}\|_{H^1(\Omega)} \le C_\alpha$.

Proof. The variational form for the problem (3.24),

$$a(u,v) = \int_\Omega \left(\tfrac{1}{2}\nabla u(r_1,r_2)\cdot\nabla v(r_1,r_2) + (\kappa(r_1)+\kappa(r_2))\,u(r_1,r_2)\,v(r_1,r_2)\right)\,dr_1dr_2, \tag{3.29}$$

is bounded on $H^1_0(\Omega)$ because of the Hardy inequality

$$\int_0^\infty (u(r)/r)^2\,dr \le 4\int_0^\infty (u'(r))^2\,dr \tag{3.30}$$

for $u \in H^1_0(0,\infty)$.

The form (3.29) is coercive on $H^1_0(\Omega)$, since $\kappa(r_1)+\kappa(r_2) \ge \frac{1}{2}$. In particular,

$$a(v,v) \ge \frac{1}{2}\int_\Omega |\nabla v(r_1,r_2)|^2 + v(r_1,r_2)^2\,dr_1dr_2, \tag{3.31}$$

for all $v \in H^1_0(\Omega)$. Note that

$$-\frac{1}{2}\frac{d^2}{dr^2} + \frac{1}{r^2} - \frac{1}{r} \ge -\frac{1}{8} \text{ on } H^1_0(0,\infty),$$

since the operator on the left-hand side is the case $\ell = 1$ of the radial Schrödinger operator

$$-\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} - \frac{1}{r}$$

for the hydrogen atom for the orbital quantum number ℓ. Thus

$$a(v,v) \geq \frac{3}{4}\int_\Omega v(r_1,r_2)^2\,dr_1dr_2. \tag{3.32}$$

Thus there is a unique distributional solution $T \in H_0^1(\Omega)$ to (3.24), satisfying

$$a(T,v) = -\int_\Omega r_1^2 r_2^2 \hat{\psi}_0(r_1,r_2)v(r_1,r_2)\,dr_1dr_2 \tag{3.33}$$

for all $v \in H_0^1(\Omega)$.

Now let us consider the exponential decay. For simplicity, we will use the notation $\mathbf{r} = (r_1, r_2)$ for points in Ω. Let $v, w \in C_0^\infty(\Omega)$. Differentiating, we find

$$\nabla\big(e^{\alpha(r_1+r_2)}v(\mathbf{r})\big)\cdot\nabla w(\mathbf{r}) = e^{\alpha(r_1+r_2)}\Big(\alpha v(\mathbf{r})\Big(\frac{\partial w}{\partial r_1}(\mathbf{r}) + \frac{\partial w}{\partial r_2}(\mathbf{r})\Big) + \nabla v(\mathbf{r})\cdot\nabla w(\mathbf{r})\Big). \tag{3.34}$$

Applying (3.34) twice yields

$$\begin{aligned}&\nabla\left(e^{\alpha(r_1+r_2)}v(\mathbf{r})\right)\cdot\nabla w(\mathbf{r}) - \nabla v(\mathbf{r})\cdot\nabla\left(e^{\alpha(r_1+r_2)}w(\mathbf{r})\right)\\ &= \alpha e^{\alpha(r_1+r_2)}\Big(v(\mathbf{r})\Big(\frac{\partial w}{\partial r_1}(\mathbf{r}) + \frac{\partial w}{\partial r_2}(\mathbf{r})\Big) - w(\mathbf{r})\Big(\frac{\partial v}{\partial r_1}(\mathbf{r}) + \frac{\partial v}{\partial r_2}(\mathbf{r})\Big)\Big).\end{aligned} \tag{3.35}$$

Thus an integration by parts shows that

$$\begin{aligned}&\int_\Omega \nabla\left(e^{\alpha(r_1+r_2)}v(\mathbf{r})\right)\cdot\nabla w(\mathbf{r})\,d\mathbf{r} - \int_\Omega \nabla v(\mathbf{r})\cdot\nabla\left(e^{\alpha(r_1+r_2)}w(\mathbf{r})\right)\,d\mathbf{r}\\ &= \int_\Omega 2\alpha e^{\alpha(r_1+r_2)}v(\mathbf{r})\Big(\frac{\partial w}{\partial r_1}(\mathbf{r}) + \frac{\partial w}{\partial r_2}(\mathbf{r})\Big)\,d\mathbf{r} + \int_\Omega 2\alpha^2 e^{\alpha(r_1+r_2)}w(\mathbf{r})v(\mathbf{r})\,d\mathbf{r}.\end{aligned} \tag{3.36}$$

For $u(\mathbf{r}) = e^{\alpha(r_1+r_2)}v(\mathbf{r})$, we find

$$\begin{aligned}\int_\Omega \nabla u(\mathbf{r})\cdot\nabla w(\mathbf{r})\,d\mathbf{r} &= \int_\Omega \nabla v(\mathbf{r})\cdot\nabla\left(e^{\alpha(r_1+r_2)}w(\mathbf{r})\right)\,d\mathbf{r}\\ &+ \int_\Omega 2\alpha u(\mathbf{r})\Big(\frac{\partial w}{\partial r_1}(\mathbf{r}) + \frac{\partial w}{\partial r_2}(\mathbf{r})\Big)\,d\mathbf{r} + \int_\Omega 2\alpha^2 w(\mathbf{r})u(\mathbf{r})\,d\mathbf{r}.\end{aligned} \tag{3.37}$$

Therefore

$$a(u,w) = a(v, e^{\alpha(r_1+r_2)}w(\mathbf{r})) + \int_\Omega \alpha u(\mathbf{r})\Big(\frac{\partial w}{\partial r_1}(\mathbf{r}) + \frac{\partial w}{\partial r_2}(\mathbf{r})\Big)\,d\mathbf{r} + \int_\Omega \alpha^2 w(\mathbf{r})u(\mathbf{r})\,d\mathbf{r}. \tag{3.38}$$

Define the bilinear form

$$a_\alpha(v,w) = a(v,w) - \int_\Omega \alpha v(\mathbf{r})\Big(\frac{\partial w}{\partial r_1}(\mathbf{r}) + \frac{\partial w}{\partial r_2}(\mathbf{r})\Big)\,d\mathbf{r} - \int_\Omega \alpha^2 v(\mathbf{r})w(\mathbf{r})\,d\mathbf{r}. \tag{3.39}$$

Then for $u(\mathbf{r}) = e^{\alpha(r_1+r_2)}v(\mathbf{r})$, we find

$$a_\alpha(u,w) = a(v, e^{\alpha(r_1+r_2)}w(\mathbf{r})). \tag{3.40}$$

All of the above relations extend to the case where u, v, and w are in $H_0^1(\Omega)$.

For α sufficiently small, a_α is coercive on $H_0^1(\Omega)$ because (3.32) implies

$$a_\alpha(v,v) = a(v,v) - \int_\Omega \alpha^2 v(\mathbf{r})^2\,d\mathbf{r} \geq \int_\Omega \Big(\frac{3}{4} - \alpha^2\Big)v(r_1,r_2)^2\,dr_1dr_2. \tag{3.41}$$

Thus a_α is coercive for $0 \le \alpha < \frac{1}{2}\sqrt{3}$. Clearly a_α is continuous on $H^1_0(\Omega)$ for $0 \le \alpha < \frac{1}{2}\sqrt{3}$, so the Lax-Milgram theorem implies that there is a unique $u \in H^1_0(\Omega)$ such that

$$a_\alpha(u, w) = -\int_\Omega r_1^2 r_2^2 \hat{\psi}_0(\mathbf{r}) e^{\alpha(r_1+r_2)} w(\mathbf{r})\, d\mathbf{r} \tag{3.42}$$

for all $w \in H^1_0(\Omega)$. Define $v(\mathbf{r}) = e^{-\alpha(r_1+r_2)}u(\mathbf{r})$ for $\mathbf{r} \in \Omega$. Then $v \in H^1_0(\Omega)$ and from (3.40) we find

$$a(v, e^{\alpha(r_1+r_2)}w(\mathbf{r})) = -\int_\Omega r_1^2 r_2^2 \hat{\psi}_0(\mathbf{r}) e^{\alpha(r_1+r_2)} w(\mathbf{r})\, d\mathbf{r} = a(T, e^{\alpha(r_1+r_2)}w(\mathbf{r})) \tag{3.43}$$

for all $w \in C^\infty_0(\Omega)$. Thus we conclude that $v = T$ and so

$$\|e^{\alpha(r_1+r_2)}T\|_{H^1(\Omega)} = \|u\|_{H^1(\Omega)} \le C_\alpha \|r_1^2 r_2^2 \hat{\psi}_0(\mathbf{r}) e^{\alpha(r_1+r_2)}\|_{L^2(\Omega)} \le C'_\alpha. \quad \textbf{QED} \tag{3.44}$$

Note that (3.44) implies that

$$\|e^{\alpha(r_1+r_2)}T\|_{L^p(\Omega)} \le C_{p,\alpha} \tag{3.45}$$

for all $p < \infty$ and $0 \le \alpha < \frac{1}{2}\sqrt{3}$ [20].

With ψ' as defined in (3.28), we have

$$\int_{\mathbb{R}^6} |\psi'|^2\, d\mathbf{r}_1\, d\mathbf{r}_2 = \frac{32\pi^2}{3} \int_\Omega T^2\, dr_1 dr_2, \tag{3.46}$$

where the constant $32\pi^2/3$ comes from (3.21).

3.4. An approximation scheme. We used a Galerkin scheme to compute the solution of (3.24). Consider the Laguerre functions $\sigma_{n,\alpha}(r) = e^{-\alpha r} r^n$ [14, 21]. We used tensor products of these functions for $\alpha = 1$, which we denote by $\sigma_n = \sigma_{n,1}$, to approximate the solution of (3.24):

$$v_k(r_1, r_2) = \sum_{i=1}^{k} \sum_{j=1}^{k} c_{ij} \sigma_i(r_1) \sigma_j(r_2). \tag{3.47}$$

Using the variational form (3.29), we seek solutions u_k of the form (3.47) to

$$a(u_k, v_k) = (f, v_k) \tag{3.48}$$

for all v_k of the form (3.47), where

$$(f, v_k) = \int_0^\infty \int_0^\infty f(r_1, r_2) v_k(r_1, r_2)\, dr_1 dr_2. \tag{3.49}$$

In particular, we will be interested in the case

$$f(r_1, r_2) = -\sigma_2(r_1)\sigma_2(r_2), \tag{3.50}$$

so the computation of the integrals on the right-hand side in (3.48) are simplified. The solution T_k of (3.48) using $k = 9$ is depicted in Figure 3.2.

Note that $\int_{\mathbb{R}^3} \sigma_0(|\mathbf{r}|)^2\, d\mathbf{r} = 4\pi \int_0^\infty \sigma_1(r)^2\, dr = \pi$. Thus we can write $\hat{\psi}_0(r_1, r_2) = (1/\pi)\sigma_0(r_1)\sigma_0(r_2)$. In view of (3.26) and (3.57), we have

$$C_6 = -\frac{32\pi}{3} \int_0^\infty \int_0^\infty \sigma_2(r_1)\sigma_2(r_2) T(r_1, r_2)\, dr_1 dr_2. \tag{3.51}$$

Similarly, we can write

$$C_6 = \frac{32\pi^2}{3} a(T, T), \tag{3.52}$$

where $a(\cdot, \cdot)$ is the form defined in (3.29). In Table 3.1, we see values of C_6 computed using Laguerre functions of degree k for $k = 2, \ldots, 15$ via the formula (3.51). For values of $k \ge 12$, we begin to see effects of round-off. For C_6 values with $k \ge 9$ we have agreement with [4].

k	C_6 values	k	C_6 values	k	C_6 values
		6	6.499025	11	6.49902670534
2	6.17	7	6.4990266	12	6.49902670539
3	6.486	8	6.49902669	13	6.499026705401
4	6.4985	9	6.499026703	14	6.499026705404
5	6.49900	10	6.4990267051	15	6.499026705403

TABLE 3.1

Convergence of C_6 values as a function of the degree k of polynomials used in the Laguerre function approximation.

3.5. Spherical harmonics calculations. We collect some facts about spherical harmonics that will be used for two concrete calculations as well as subsequently in Section 4. We denote by $(\mathcal{Y}_l^m)_{l\in\mathbb{N},\,-l\le m\le l}$ the basis of *real* spherical harmonics [24], with the normalization convention that $(\mathcal{Y}_l^m)_{l\in\mathbb{N},\,-l\le m\le l}$ is an orthonormal basis of $L^2(\mathbb{S}_2)$. In particular,

$$\forall \mathbf{s}=(x,y,z)\in\mathbb{S}_2,\quad \mathcal{Y}_0^0(x,y,z)=\frac{1}{\sqrt{4\pi}},\quad \mathcal{Y}_1^{-1}(x,y,z)=\sqrt{\frac{3}{4\pi}}\,x,$$
$$\mathcal{Y}_1^0(x,y,z)=\sqrt{\frac{3}{4\pi}}\,z,\quad \mathcal{Y}_1^1(x,y,z)=\sqrt{\frac{3}{4\pi}}\,y.$$

The fundamental remark is that

$$\forall \mathbf{s}\in\mathbb{S}_2,\quad \mathbf{s}=\left(\frac{4\pi}{3}\right)^{1/2}\sum_{-1\le m\le 1}\mathcal{Y}_1^m(\mathbf{s})\mathbf{e}_m,$$

where $\mathbf{e}_{-1}:=\mathbf{e}_x$, $\mathbf{e}_0:=\mathbf{e}_z$, $\mathbf{e}_1:=\mathbf{e}_y$, so that the function b has a simple expression in terms of spherical harmonics:

$$\begin{aligned} b(\mathbf{s}_1,\mathbf{s}_2)&=\mathbf{s}_1\cdot\mathbf{s}_2-3(\mathbf{s}_1\cdot\mathbf{e})(\mathbf{s}_2\cdot\mathbf{e})\\ &=\frac{4\pi}{3}\Big(\sum_{-1\le m\le 1}\mathcal{Y}_1^m(\mathbf{s}_1)\,\mathcal{Y}_1^m(\mathbf{s}_2)-3\Big(\sum_{-1\le m\le 1}\mathcal{Y}_1^m(\mathbf{s}_1)\mathbf{e}_m\cdot\mathbf{e}\Big)\Big(\sum_{-1\le m\le 1}\mathcal{Y}_1^m(\mathbf{s}_2)\mathbf{e}_m\cdot\mathbf{e}\Big)\Big). \end{aligned}\tag{3.53}$$

We can simplify by assuming, without loss of generality, that $\mathbf{e}_0:=\mathbf{e}$. In this case, b simplifies to

$$b(\mathbf{s}_1,\mathbf{s}_2)=\frac{4\pi}{3}\Big(\sum_{-1\le m\le 1}\mathcal{Y}_1^m(\mathbf{s}_1)\,\mathcal{Y}_1^m(\mathbf{s}_2)-3\mathcal{Y}_1^0(\mathbf{s}_1)\mathcal{Y}_1^0(\mathbf{s}_2)\Big).\tag{3.54}$$

Using the orthonormality property

$$\int_{\mathbb{S}_2}\mathcal{Y}_l^m(\mathbf{s})\mathcal{Y}_{l'}^{m'}(\mathbf{s})\,d\mathbf{s}=\delta_{l,l'}\delta_{m,m'},$$

we obtain

$$\int_{(\mathbb{S}_2)^2}b(\mathbf{s}_1,\mathbf{s}_2)\mathcal{Y}_{l_1}^{m_1}(\mathbf{s}_1)\mathcal{Y}_{l_2}^{m_2}(\mathbf{s}_2)\,d\mathbf{s}_1\,d\mathbf{s}_2=\frac{4\pi}{3}\delta_{1,l_1}\delta_{1,l_2}\left(\delta_{m_1,m_2}-3\delta_{0,m_1}\delta_{0,m_2}\right).\tag{3.55}$$

Therefore

$$\int_{(\mathbb{S}_2)^2}b(\mathbf{s}_1,\mathbf{s}_2)\sum_{-1\le m\le 1}\mathcal{Y}_1^m(\mathbf{s}_1)\,\mathcal{Y}_1^m(\mathbf{s}_2)\,d\mathbf{s}_1\,d\mathbf{s}_2=0.\tag{3.56}$$

Thus

$$\begin{aligned}\int_{{\mathbb{S}_2}^2} b(\mathbf{s}_1,\mathbf{s}_2)^2\,d\mathbf{s}_1\,d\mathbf{s}_2 &= -4\pi\int_{{\mathbb{S}_2}^2} b(\mathbf{s}_1,\mathbf{s}_2)\mathcal{Y}_1^0(\mathbf{s}_1)\mathcal{Y}_1^0(\mathbf{s}_2)\\ &= -\frac{(4\pi)^2}{3}\left(\delta_{0,0}-3\delta_{0,0}\delta_{0,0}\right) = \frac{32\pi^2}{3}.\end{aligned} \tag{3.57}$$

This proves (3.21).

3.6. Asymptotic electron distributions. Knowing the exact form of the wave function perturbation allows us to compute, at least asymptotically, properties of the wave function of physical interest. First of all, the electron distribution is given by

$$\begin{aligned}\rho_\epsilon(\mathbf{r}_1) &= 2\int_{\mathbb{R}^3}|\psi_\epsilon(\mathbf{r}_1,\mathbf{r}_2)|^2\,d\mathbf{r}_2 = 2\int_{\mathbb{R}^3}|\psi_\epsilon(\mathbf{r}_2,\mathbf{r}_1)|^2\,d\mathbf{r}_2 = 2\int_{\mathbb{R}^3}|\psi_0(\mathbf{r}_1,\mathbf{r}_2)+\epsilon\psi'(\mathbf{r}_1,\mathbf{r}_2)|^2\,d\mathbf{r}_2+\mathrm{o}(\epsilon)\\ &= 2\int_{\mathbb{R}^3}|\psi_0(\mathbf{r}_1,\mathbf{r}_2)|^2\,d\mathbf{r}_2+4\epsilon\int_{\mathbb{S}_2}\int_0^\infty\psi_0(\mathbf{r}_1,r\mathbf{s})b(|\mathbf{r}_1|^{-1}\mathbf{r}_1,\mathbf{s})T(|\mathbf{r}_1|,r)|\mathbf{r}_1|^{-1}r\,dr\,d\mathbf{s}+\mathrm{o}(\epsilon)\\ &= \rho_0(\mathbf{r}_1)+4\epsilon\int_0^\infty\left(\int_{\mathbb{S}_2}b(|\mathbf{r}_1|^{-1}\mathbf{r}_1,\mathbf{s})\,d\mathbf{s}\right)\psi_0(\mathbf{r}_1,r\mathbf{s})T(|\mathbf{r}_1|,r)|\mathbf{r}_1|^{-1}r\,dr+\mathrm{o}(\epsilon)\\ &= \rho_0(\mathbf{r}_1)+\mathrm{o}(\epsilon)\end{aligned} \tag{3.58}$$

since $\psi_0(\mathbf{r}_1,r\mathbf{s})$ is independent of $\mathbf{s}$ and the angular integral vanishes. Thus to first order, the electron distribution is unchanged for large R (small ϵ).

We can also determine the asymptotic dipole associated with ψ' in the following sense. Using the idea of "atoms in molecules" [18], we can associate a half-space $\mathbb{H}_i$ to the i-th hydrogen atom, where

$$\mathbb{H}_i = \left\{\mathbf{R}\in\mathbb{R}^3\,:\,(-1)^iR_1>0\right\}.$$

The "local" dipoles $\mathbf{D}_i$ associated with the i-th hydrogen atom are defined to be the vectors

$$\mathbf{D}_1 = 2\int_{\mathbb{H}_1\times\mathbb{R}^3}\mathbf{r}_1|\psi_\epsilon(\mathbf{r}_1,\mathbf{r}_2)|^2\,d\mathbf{r}_1\,d\mathbf{r}_2,\quad \mathbf{D}_2 = 2\int_{\mathbb{R}^3\times\mathbb{H}_2}\mathbf{r}_2|\psi_\epsilon(\mathbf{r}_1,\mathbf{r}_2)|^2\,d\mathbf{r}_1\,d\mathbf{r}_2. \tag{3.59}$$

Writing $\psi_\epsilon\approx\psi_0+\epsilon\psi'$, we find

$$\mathbf{D}_i \approx 4\epsilon\int_{\mathbb{R}^3\times\mathbb{R}^3}\mathbf{r}_i\psi_0(\mathbf{r}_1,\mathbf{r}_2)\psi'(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2, \tag{3.60}$$

since the integrands are exponentially small on the complement of $\mathbb{H}_1\times\mathbb{R}^3$ and $\mathbb{R}^3\times\mathbb{H}_2$ and

$$\int_{\mathbb{R}^3\times\mathbb{R}^3}\mathbf{r}_i|\psi_0(\mathbf{r}_1,\mathbf{r}_2)|^2\,d\mathbf{r}_1\,d\mathbf{r}_2 = 0, \tag{3.61}$$

by symmetry. But

$$\begin{aligned}&\int_{\mathbb{R}^3\times\mathbb{R}^3}\mathbf{r}_i\psi_0(\mathbf{r}_1,\mathbf{r}_2)\psi'(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2\\ &= \frac{1}{\pi}\int_{\mathbb{R}^3\times\mathbb{R}^3}\mathbf{r}_i e^{-|\mathbf{r}_1|-|\mathbf{r}_2|}T(|\mathbf{r}_1|,|\mathbf{r}_2|)|\mathbf{r}_1|^{-2}|\mathbf{r}_2|^{-2}\mathcal{B}(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2\\ &= \frac{1}{\pi}\int_{{\mathbb{S}_2}^2}\mathbf{s}_i b(\mathbf{s}_1,\mathbf{s}_2)\int_\Omega r_i e^{-r_1-r_2}T(r_1,r_2)r_1\,r_2\,dr_1\,dr_2\,d\mathbf{s}_1\,d\mathbf{s}_2,\end{aligned} \tag{3.62}$$

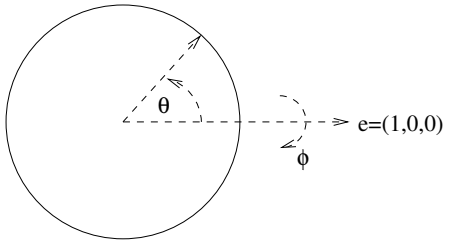

FIG. 3.4. *Spherical coordinates for visualizing the function b defined in* (3.16).

where $\mathbf{s}_i = |\mathbf{r}_i|^{-1}\mathbf{r}_i$ and $r_i = |\mathbf{r}_i|$. We can compute the angular integral using (3.54). Without loss of generality, we can assume that $i = 1$. Then for $\mu \in \{-1, 0, 1\}$,

$$\begin{aligned}\int_{\mathbb{S}_2} \mathcal{Y}_1^\mu(\mathbf{s}_1) b(\mathbf{s}_1, \mathbf{s}_2)\, d\mathbf{s}_1 &= \frac{4\pi}{3} \int_{{\mathbb{S}_2}^2} \mathcal{Y}_1^\mu(\mathbf{s}_1) \Big(\sum_{-1\le m\le 1} \mathcal{Y}_1^m(\mathbf{s}_1)\, \mathcal{Y}_1^m(\mathbf{s}_2) - 3\mathcal{Y}_1^0(\mathbf{s}_1)\mathcal{Y}_1^0(\mathbf{s}_2)\Big)\, d\mathbf{s}_1 \\ &= \frac{4\pi}{3}\big(\mathcal{Y}_1^\mu(\mathbf{s}_2) - 3\delta_{\mu,0}\mathcal{Y}_1^0(\mathbf{s}_2)\big).\end{aligned} \tag{3.63}$$

But by symmetry, the integrals of each $\mathcal{Y}_1^m$ are zero for all $m \in \{-1, 0, 1\}$. So

$$\int_{{\mathbb{S}_2}^2} \mathbf{s}_i\, b(\mathbf{s}_1, \mathbf{s}_2)\, d\mathbf{s}_1\, d\mathbf{s}_2 = 0. \tag{3.64}$$

Thus we find that, to order ϵ, the dipole is zero. This confirms that the van der Waals interaction between hydrogen atoms cannot be explained as a classical (induced) dipole-dipole interaction.

3.7. Visualizing $\mathcal{B}$. We can represent the coordinates for $\mathbb{S}_2$ via

$$\mathbf{s}(\theta, \phi) = (\cos\theta, \sin\theta\, \cos\phi, \sin\theta\, \sin\phi)$$

where $-\pi/2 < \theta \le \pi/2$ and $-\pi < \phi \le \pi$. With this representation,

$$d\mathbf{s} = \sin\theta\, d\phi\, d\theta.$$

Although the ϕ variable is important, we are mainly interested to see if there are correlations between the θ variables. Thus we will average out the ϕ variables to simplify. Define

$$\beta(\theta_1, \theta_2) = \sin\theta_1 \sin\theta_2 \int_{[-\pi,\pi]^2} b(\mathbf{s}(\theta_1, \phi_1), \mathbf{s}(\theta_2, \phi_2))\, d\phi_1\, d\phi_2\,.$$

Then for any function f defined on $\mathbb{S}_2 \times \mathbb{S}_2$ that is cylindrically symmetric around the x-axis (that is, the axis joining the two hydrogen atoms), we have

$$\int_{\mathbb{S}_2\times\mathbb{S}_2} f(\mathbf{s}_1, \mathbf{s}_2) b(\mathbf{s}_1, \mathbf{s}_2)\, d\mathbf{s}_1 d\mathbf{s}_2 = \int_{[-\pi/2,\pi/2]^2} f(\theta_1, \theta_2)\beta(\theta_1, \theta_2)\, d\theta_1 d\theta_2$$

since f does not depend on ϕ_1, ϕ_2. In these coordinates,

$$b(\mathbf{s}(\theta_1, \phi_1), \mathbf{s}(\theta_2, \phi_2)) = \sin\theta_1 \sin\theta_2\, (\cos\phi_1\, \cos\phi_2 + \sin\phi_1\, \sin\phi_2) - 2\cos\theta_1 \cos\theta_2\,.$$

Thus

$$\beta(\theta_1, \theta_2) = -8\pi^2 \sin\theta_1 \sin\theta_2 \cos\theta_1 \cos\theta_2 = -2\pi^2 \sin 2\theta_1 \sin 2\theta_2\,.$$

Recalling that $T < 0$, we have a positive correlation when $\mathrm{sign}(\theta_1) = \mathrm{sign}(\theta_2)$ and a negative correlation otherwise.

4. Proof of Theorem 3.1. Let $\Omega = (0,+\infty)^2$ and T be the unique solution of (3.24) as guaranteed by Lemma 3.2. Then T is the unique solution of the minimization problem

$$T := \operatorname*{argmin}_{u\in H^1_0(\Omega)} \left(\frac{1}{2}\int_\Omega |\nabla u|^2 + \int_\Omega (\kappa(r_1)+\kappa(r_2))u(r_1,r_2)^2\,dr_1\,dr_2 + \int_\Omega r_1^2 r_2^2 e^{-(r_1+r_2)} u(r_1,r_2)\,dr_1\,dr_2 \right), \tag{4.1}$$

where κ is defined in (3.25). Note that T satisfies, for all $u \in H^1_0(\Omega)$,

$$a(T,u) = \frac{1}{\pi}\int_\Omega r_1^2 r_2^2 e^{-(r_1+r_2)} u(r_1,r_2)\,dr_1\,dr_2, \tag{4.2}$$

where the bilinear form $a(\cdot,\cdot)$ is defined in (3.29).

We now introduce the function ζ defined almost everywhere in $\mathbb{R}^3\times\mathbb{R}^3$ by

$$\zeta(\mathbf{r}_1,\mathbf{r}_2) = \frac{T(r_1,r_2)}{r_1^2 r_2^2}\mathcal{B}(\mathbf{r}_1,\mathbf{r}_2) = \frac{T(r_1,r_2)}{r_1 r_2} b(\mathbf{s}_1,\mathbf{s}_2), \tag{4.3}$$

where $\mathbf{s}_i = (1/r_i)\mathbf{r}_i$. The function ζ is in $L^2(\mathbb{R}^3\times\mathbb{R}^3)$, and we have

$$\int_{\mathbb{R}^3\times\mathbb{R}^3} |\zeta(\mathbf{r}_1,\mathbf{r}_2)|^2\,d\mathbf{r}_1\,d\mathbf{r}_2 = \left(\int_{(\mathbb{S}_2)^2} |b(\mathbf{s}_1,\mathbf{s}_2)|^2\,d\mathbf{s}_1\,d\mathbf{s}_2\right)\left(\int_\Omega |T(r_1,r_2)|^2\,dr_1\,dr_2\right) = \frac{2}{3}(4\pi)^2\|T\|^2_{L^2(\Omega)}, \tag{4.4}$$

$$\int_{\mathbb{R}^3\times\mathbb{R}^3} \zeta(\mathbf{r}_1,\mathbf{r}_2)\psi_0(\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2 = \int_\Omega T(r_1,r_2)\frac{e^{-(r_1+r_2)}}{\pi} r_1 r_2\,dr_1\,dr_2 \int_{(\mathbb{S}_2)^2} b(\mathbf{s}_1,\mathbf{s}_2)\,d\mathbf{s}_1\,d\mathbf{s}_2 = 0. \tag{4.5}$$

Similarly, by Hardy's inequality

$$\int_{\mathbb{R}^3\times\mathbb{R}^3} r_i^{-2}\zeta^2\,d\mathbf{r}_1\,d\mathbf{r}_2 \le C\int_\Omega r_i^{-2}T^2\,dr_1\,dr_2 \le C'\int_\Omega T_{,i}^2\,dr_1\,dr_2 \le C''. \tag{4.6}$$

The next step is to show that

$$-\frac{1}{2}\Delta\zeta = \frac{\zeta}{r_1} + \frac{\zeta}{r_2} + \lambda_0\zeta - \psi_0\mathcal{B} \tag{4.7}$$

in the distributional sense, where Δ denotes the usual Laplacian in $\mathbb{R}^6$. Note that the right-hand side is in $L^2(\mathbb{R}^3\times\mathbb{R}^3)$ in view of (4.6).

Let $\phi \in C^\infty_{\rm c}(\mathbb{R}^3\times\mathbb{R}^3)$. The function ϕ can be expanded as follows

$$\phi(\mathbf{r}_1,\mathbf{r}_2) = \sum_{l_1,l_2=0}^{+\infty} \sum_{\substack{-l_1\le m_1\le l_1\\ -l_2\le m_2\le l_2}} \phi_{l_1,m_1;l_2,m_2}(r_1,r_2)\,\mathcal{Y}_{l_1}^{m_1}(\mathbf{s}_1)\,\mathcal{Y}_{l_2}^{m_2}(\mathbf{s}_2),$$

where the functions $\phi_{l_1,m_1;l_2,m_2}$ are defined by

$$\phi_{l_1,m_1;l_2,m_2}(r_1,r_2) = \int_{\mathbb{S}_2\times\mathbb{S}_2} \phi(r_1\mathbf{s}_1, r_2\mathbf{s}_2)\,\mathcal{Y}_{l_1}^{m_1}(\mathbf{s}_1)\,\mathcal{Y}_{l_2}^{m_2}(\mathbf{s}_2)\,d\mathbf{s}_1\,d\mathbf{s}_2. \tag{4.8}$$

Thus the functions $\phi_{l_1,m_1;l_2,m_2}$ are in $C^\infty_{\rm c}(\overline{\Omega})$, the series in the RHS being uniformly convergent, and convergent in any Sobolev space $H^s(\mathbb{R}^3\times\mathbb{R}^3)$, $s\in\mathbb{R}$. In particular,

$$\Delta\phi(\mathbf{r}_1,\mathbf{r}_2) = \sum_{l_1,l_2=0}^{+\infty} \sum_{\substack{-l_1\le m_1\le l_1\\ -l_2\le m_2\le l_2}} \left(\frac{1}{r_1}\frac{\partial^2}{\partial r_1^2}(r_1\phi_{l_1,m_1;l_2,m_2}) + \frac{1}{r_2}\frac{\partial^2}{\partial r_2^2}(r_2\phi_{l_1,m_1;l_2,m_2}) + \left(\frac{q(l_1)}{r_1^2} + \frac{q(l_2)}{r_2^2}\right)\phi_{l_1,m_1;l_2,m_2}\right)(r_1,r_2)\,\mathcal{Y}_{l_1}^{m_1}(\mathbf{s}_1)\,\mathcal{Y}_{l_2}^{m_2}(\mathbf{s}_2), \tag{4.9}$$

where $q(\ell) = \ell(\ell+1)$. We have, using (3.55) and (4.3),

$$\begin{aligned}
\langle \Delta\zeta, \phi\rangle = \langle \zeta, \Delta\phi\rangle &= \int_{\mathbb{R}^3\times\mathbb{R}^3} \zeta\, \Delta\phi \, d\mathbf{r}_1\, d\mathbf{r}_2 = \int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{T(r_1,r_2)}{r_1 r_2} b(\mathbf{s}_1,\mathbf{s}_2)\, \Delta\phi \, d\mathbf{r}_1\, d\mathbf{r}_2 \\
&= \frac{4\pi}{3} \sum_{\substack{-1\le m_1\le 1\\ -1\le m_2\le 1}} (\delta_{m_1,m_2} - 3(\mathbf{e}_{m_1}\cdot\mathbf{e})(\mathbf{e}_{m_2}\cdot\mathbf{e})) \int_\Omega r_1 r_2 T(r_1,r_2) \times \\
&\left(\frac{1}{r_1}\frac{\partial^2}{\partial r_1^2}(r_1\phi_{1,m_1;1,m_2}) + \frac{1}{r_2}\frac{\partial^2}{\partial r_2^2}(r_2\phi_{1,m_1;1,m_2}) + \left(\frac{q(1)}{r_1^2}+\frac{q(1)}{r_2^2}\right)\phi_{1,m_1;1,m_2}\right) dr_1\, dr_2 \\
&= \frac{4\pi}{3} \sum_{\substack{-1\le m_1\le 1\\ -1\le m_2\le 1}} (\delta_{m_1,m_2} - 3(\mathbf{e}_{m_1}\cdot\mathbf{e})(\mathbf{e}_{m_2}\cdot\mathbf{e})) \\
&\quad \times \int_\Omega T(r_1,r_2)\left(\Delta_2 u_{m_1,m_2}(r_1,r_2) + \left(\frac{2}{r_1^2}+\frac{2}{r_2^2}\right) u_{m_1,m_2}(r_1,r_2)\right) dr_1\, dr_2,
\end{aligned}$$

where we have introduced the functions $u_{m_1,m_2}(r_1,r_2) = r_1 r_2 \phi_{1,m_1;1,m_2}(r_1,r_2)$. As the latter functions are in $H_0^1(\Omega)\cap C_c^\infty(\overline{\Omega})$, we infer from (4.2) that for each $-1 \le m_1, m_2 \le 1$,

$$\begin{aligned}
&\int_\Omega T(r_1,r_2)\left(\Delta_2 u_{m_1,m_2}(r_1,r_2) + \left(\frac{2}{r_1^2}+\frac{2}{r_2^2}\right) u_{m_1,m_2}(r_1,r_2)\right) dr_1\, dr_2 \\
&= -\int_\Omega \nabla T\cdot\nabla u_{m_1,m_2}\, dr_1\, dr_2 + \int_\Omega \left(\frac{2}{r_1^2}+\frac{2}{r_2^2}\right) T(r_1,r_2) u_{m_1,m_2}(r_1,r_2)\, dr_1\, dr_2 \\
&= -2\int_\Omega \left(\left(\frac{1}{r_1}+\frac{1}{r_2}+\lambda_0\right) T(r_1,r_2) - r_1^2 r_2^2 e^{-(r_1+r_2)}\right) u_{m_1,m_2}(r_1,r_2)\, dr_1\, dr_2 \\
&= -2\int_\Omega \left(\left(\frac{1}{r_1}+\frac{1}{r_2}+\lambda_0\right) T(r_1,r_2) - r_1^2 r_2^2 e^{-(r_1+r_2)}\right) r_1 r_2 \phi_{1,m_1;1,m_2}(r_1,r_2)\, dr_1\, dr_2.
\end{aligned}$$

Therefore,

$$\begin{aligned}
\langle \Delta\zeta, \phi\rangle &= -2\times\frac{4\pi}{3} \sum_{\substack{-1\le m_1\le 1\\ -1\le m_2\le 1}} (\delta_{m_1,m_2} - 3(\mathbf{e}_{m_1}\cdot\mathbf{e})(\mathbf{e}_{m_2}\cdot\mathbf{e})) \\
&\quad \times \int_\Omega \left(\left(\frac{1}{r_1}+\frac{1}{r_2}+\lambda_0\right) T(r_1,r_2) - r_1^2 r_2^2 e^{-(r_1+r_2)}\right) r_1 r_2 \phi_{1,m_1;1,m_2}(r_1,r_2)\, dr_1\, dr_2 \\
&= -2\left(\int_{\mathbb{R}^3\times\mathbb{R}^3} \zeta\left(\frac{1}{r_1}+\frac{1}{r_2}+\lambda_0\right)\phi\, d\mathbf{r}_1\, d\mathbf{r}_2 - \int_{\mathbb{R}^3\times\mathbb{R}^3} \mathcal{B}\psi_0\phi\, d\mathbf{r}_1\, d\mathbf{r}_2\right).
\end{aligned} \tag{4.10}$$

Hence, (4.7) is proved. As the RHS of (4.7) is in $L^2(\mathbb{R}^3\times\mathbb{R}^3)$, so is the LHS. Consequently, $\zeta \in H^2(\mathbb{R}^3\times\mathbb{R}^3) = D(H_0)$ (the domain of the self-adjoint operator H_0), and it holds that

$$(H_0 - \lambda_0)\zeta = -\mathcal{B}\psi_0.$$

By (4.5), ζ is orthogonal to ψ_0 in $L^2(\mathbb{R}^3\times\mathbb{R}^3)$, and we finally obtain that $\zeta = \psi'$.

5. Rigorous justification of the perturbation method. The following is the main result of the paper.

THEOREM 5.1. *Let $\psi_\epsilon \in H^2(\mathbb{R}^6)$ be the positive $L^2(\mathbb{R}^6)$-normalized ground state of H^ϵ and let λ_ϵ be the associated ground-state energy (solutions of* (1.4)*). Let (ψ_0,λ_0) be as given in* (1.7)*, and let $\psi' \in H^2(\mathbb{R}^6)$ be the unique solution to* (3.28)*. Then*

$$\begin{aligned}
\|\psi_\epsilon - \psi_0 - \epsilon\psi'\|_{H^2(\mathbb{R}^6)} &\le C\epsilon^{4/3}(\log\epsilon)^3 \\
|\lambda_\epsilon - (\lambda_0 - C_6\epsilon^2)| &\le C\epsilon^{7/3}(\log\epsilon)^3,
\end{aligned} \tag{5.1}$$

where C_6 is given by (2.16).

Define P to be the projection onto the space spanned by ψ_0 defined in (1.7). Using the Feshbach-Schur method [8, 1], we write $\psi_\epsilon = \alpha_\epsilon \psi_0 + Y_\epsilon$, where $Y_\epsilon = P^\perp \psi_\epsilon$ and $|\alpha_\epsilon| \le 1$. We will show in Section 5.2 that $\alpha_\epsilon \neq 0$, for ϵ small enough, so we can write $Y_\epsilon = \alpha_\epsilon \widehat{Y}_\epsilon$. Then the equation (1.4) for ψ_ϵ simplifies to

$$H_\epsilon(\widehat{Y}_\epsilon + \psi_0) = \lambda_\epsilon(\widehat{Y}_\epsilon + \psi_0), \tag{5.2}$$

after dividing by α_ϵ. Multiplying on the left by $P^\perp$ we find

$$P^\perp H_\epsilon(\widehat{Y}_\epsilon + \psi_0) = \lambda_\epsilon \widehat{Y}_\epsilon,$$

and so we can characterize $\widehat{Y}_\epsilon$ by solving

$$(H_\epsilon^\perp - \lambda_\epsilon)\widehat{Y}_\epsilon = -P^\perp H_\epsilon \psi_0 = -P^\perp V_\epsilon \psi_0 = -V_\epsilon \psi_0 + \nu_\epsilon \psi_0, \quad \widehat{Y}_\epsilon \perp \psi_0, \tag{5.3}$$

where $H_\epsilon^\perp = P^\perp(H_0 + V_\epsilon)P^\perp$ and ν_ϵ is defined in (2.14). Thus $\psi_\epsilon = \alpha_\epsilon\big(\psi_0 + \widehat{Y}_\epsilon\big)$ and we can determine α_ϵ using the fact that $\|\psi_\epsilon\|_{L^2(\mathbb{R}^6)} = 1$:

$$\alpha_\epsilon^{-2} = \|\psi_0 + \widehat{Y}_\epsilon\|^2_{L^2(\mathbb{R}^6)} = \|\psi_0\|^2_{L^2(\mathbb{R}^6)} + \|\widehat{Y}_\epsilon\|^2_{L^2(\mathbb{R}^6)} = 1 + \|\widehat{Y}_\epsilon\|^2_{L^2(\mathbb{R}^6)}. \tag{5.4}$$

Remark 5.1. *The standard perturbation expansion* (2.4) *can be related simply to the Feshbach-Schur expansion as follows. The latter can be written*

$$\psi_\epsilon = \alpha_\epsilon \psi_0 + Y_\epsilon = \alpha_\epsilon \psi_0 + \epsilon \psi' + \mathcal{O}(\epsilon^{4/3}(\log \epsilon)^3), \tag{5.5}$$

where the $\mathcal{O}$ term is measured in $H^2(\mathbb{R}^6)$ and α_ϵ is defined in (5.4)*, so that using the subsequent estimate* (5.26)

$$\alpha_\epsilon = \sqrt{1 - \|Y_\epsilon\|^2_{L^2(\mathbb{R}^6)}} = 1 + \mathcal{O}(\epsilon^2). \tag{5.6}$$

Thus the two perturbation approaches are identical to within $o(\epsilon)$.

5.1. Lower bounds. In order to justify the Schur decomposition, we need to show that $H_\epsilon^\perp - \lambda_\epsilon$ is invertible on $\psi_0^\perp$, and we need some uniform bound on its inverse. It is proved in [1] that the symmetric operator $H_\epsilon^\perp - \lambda_\epsilon$ is uniformly coercive, i.e.,

$$H_\epsilon^\perp - \lambda_\epsilon \ge \gamma > 0 \text{ on } \psi_0^\perp$$

for ϵ sufficiently small and γ independent of ϵ. For completeness, we sketch this result.

Let $\gamma_1 = 3/8$ be the difference between the ground state energy and the energy of the first excited state of a hydrogen atom, that is, the second lowest eigenvalue of H_0. We know that

$$P^\perp H_0 P^\perp - \lambda_0 - \gamma_1 \ge 0 \text{ on } \psi_0^\perp.$$

We need to analyze the relevant perturbations to yield a similar result for

$$H_\epsilon^\perp - \lambda_\epsilon = P^\perp(H_0 + V_\epsilon)P^\perp - \lambda_\epsilon. \tag{5.7}$$

Let λ^- be the ground state energy of the hydrogen ion H^-. Define $\gamma_2 = \lambda^- - \lambda_0$. Let us prove that $\gamma_2 > 0$. The Hamiltonian for the hydrogen ion is

$$H^- = -\frac{1}{2}\Delta_{\mathbf{r}_1} - \frac{1}{2}\Delta_{\mathbf{r}_2} - \frac{1}{|\mathbf{r}_1|} - \frac{1}{|\mathbf{r}_2|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = H_0 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{5.8}$$

It can be shown using the HVZ theorem [19, page 120] that the hydrogen ion has a ground state, and by an analogous argument to that used for the ground state of the hydrogen molecule, it follows that the ground

state for (5.8) is non-degenerate and can be represented by an $L^2(\mathbb{R}^6)$-normalized eigenfunction Ψ^- that is positive almost everywhere. We have

$$\lambda^- = \min_{\psi\in H^1(\mathbb{R}^6)\setminus\{0\}} \frac{(\psi, H^-\psi)}{\|\psi\|^2}, \quad \Psi^- = \operatorname{argmin}\left\{(\psi, H^-\psi) \,:\, \psi\in H^1(\mathbb{R}^6),\ \|\psi\|=1,\ \psi\geq 0\right\}. \tag{5.9}$$

We necessarily have

$$\lambda_0 \leq \frac{(\Psi^-, H_0\Psi^-)}{\|\Psi^-\|^2} < \frac{(\Psi^-, H^-\Psi^-)}{\|\Psi^-\|^2} = \lambda^-, \tag{5.10}$$

since the integral

$$\int_{\mathbb{R}^6} \Psi^-(\mathbf{r}_1,\mathbf{r}_2)^2 \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\, d\mathbf{r}_1 d\mathbf{r}_2$$

must be positive. Thus $\gamma_2 = \lambda^- - \lambda_0 > 0$.

Define γ_0 by

$$\gamma_0 = \min\{\gamma_1, \gamma_2\} > 0. \tag{5.11}$$

Lemma 5.2.

$$H_\epsilon^\perp \geq \lambda_0 + \gamma_0 - \delta_\epsilon \text{ on } \psi_0^\perp, \tag{5.12}$$

where $\delta_\epsilon \to 0$ *as* $\epsilon \to 0$.

Lemma 5.2 is proved in [1], and we summarize the proof in the Appendix for completeness.

To show that $H_\epsilon^\perp - \lambda_\epsilon$ is invertible, using Lemma 5.2, we need to know that λ_ϵ is not too much greater than λ_0. But this follows just by using ψ_0 as a test function:

$$\lambda_\epsilon \leq (\psi_0, H_\epsilon\psi_0) = \lambda_0 + (\psi_0, V_\epsilon\psi_0) = \lambda_0 + \nu_\epsilon, \tag{5.13}$$

where we recall the formula (2.14) for ν_ϵ. Therefore $H_\epsilon^\perp - \lambda_\epsilon \geq \gamma_0 - \delta_\epsilon - \nu_\epsilon$ is uniformly coercive for ϵ sufficiently small.

5.2. Proof that $\alpha_\epsilon \neq 0$. If $\alpha_\epsilon = 0$, then $\psi_\epsilon = Y_\epsilon \in \psi_0^\perp$ and

$$\lambda_\epsilon = (H_\epsilon\psi_\epsilon, \psi_\epsilon) = (H_\epsilon^\perp\psi_\epsilon, \psi_\epsilon) \geq \lambda_0 + \gamma_0 - \delta_\epsilon. \tag{5.14}$$

Combining (5.14) with (5.13) we have

$$\lambda_0 + \gamma_0 - \delta_\epsilon \leq \lambda_\epsilon \leq \lambda_0 + \nu_\epsilon,$$

which gives a contradition for ϵ small enough.

5.3. Proof of Theorem 5.1. We now compare the expression (5.3) for $\widehat{Y_\epsilon}$ with one for ψ'. If ψ' is the solution to (3.4), then $\psi' \perp \psi_0$ and

$$\begin{aligned}(H_\epsilon^\perp - \lambda_\epsilon)\psi' &= P^\perp(H_0+V_\epsilon)\psi' - \lambda_\epsilon\psi' \\ &= P^\perp H_0\psi' - \lambda_0\psi' + P^\perp V_\epsilon\psi' + (\lambda_0-\lambda_\epsilon)\psi' \\ &= -P^\perp\mathcal{B}\psi_0 + P^\perp V_\epsilon\psi' + (\lambda_0-\lambda_\epsilon)\psi' \\ &= -\mathcal{B}\psi_0 + P^\perp V_\epsilon\psi' + (\lambda_0-\lambda_\epsilon)\psi'\end{aligned} \tag{5.15}$$

since $\mathcal{B}\psi_0 \perp \psi_0$. Then in view of (5.3), the difference $\mathcal{E}_\epsilon = \epsilon^{-1}\widehat{Y_\epsilon} - \psi' \in \psi_0^\perp$ satisfies

$$\begin{aligned}(H_\epsilon^\perp - \lambda_\epsilon)\mathcal{E}_\epsilon &= \epsilon^{-1}(-V_\epsilon\psi_0 + \nu_\epsilon\psi_0) + \mathcal{B}\psi_0 - P^\perp V_\epsilon\psi' - (\lambda_0-\lambda_\epsilon)\psi' \\ &= (\mathcal{B} - \epsilon^{-1}V_\epsilon)\psi_0 + \epsilon^{-1}\nu_\epsilon\psi_0 - P^\perp V_\epsilon\psi' - (\lambda_0-\lambda_\epsilon)\psi'.\end{aligned} \tag{5.16}$$

To prove that $\mathcal{E}_\epsilon \to 0$ as $\epsilon \to 0$, we use in part the following.

LEMMA 5.3. *There is a constant C independent of ϵ such that*

$$\|(\mathcal{B} - \epsilon^{-1}V_\epsilon)\psi_0\|_{L^2(\mathbb{R}^6)} \leq C\epsilon^{1/3}(\log\epsilon)^3 \tag{5.17}$$

and

$$\|V_\epsilon\,\psi'\|_{L^2(\mathbb{R}^6)} \leq C\epsilon^{1/3}. \tag{5.18}$$

We will prove this lemma in Section 5.4. Using it together with (5.16) and the bounds on $H_\epsilon^\perp$ from Section 5.1, we conclude that

$$\|\epsilon^{-1}\widehat{Y}_\epsilon - \psi'\|_{L^2(\mathbb{R}^6)} \leq C\epsilon^{1/3}|\log\epsilon|^3 + C|\lambda_0 - \lambda_\epsilon|. \tag{5.19}$$

Now let us derive an expression for the eigenvalues. From (5.2), we have

$$(H_\epsilon - \lambda_\epsilon)(\widehat{Y}_\epsilon + \psi_0) = 0.$$

Therefore

$$\begin{aligned} 0 &= ((H_\epsilon - \lambda_\epsilon)(\widehat{Y}_\epsilon + \psi_0), \psi_0) = (\widehat{Y}_\epsilon + \psi_0, (H_\epsilon - \lambda_\epsilon)\psi_0) = (\widehat{Y}_\epsilon + \psi_0, (\lambda_0 + V_\epsilon - \lambda_\epsilon)\psi_0) \\ &= (\widehat{Y}_\epsilon, V_\epsilon\psi_0) + (\lambda_0 - \lambda_\epsilon) + (\psi_0, V_\epsilon\psi_0) = (\widehat{Y}_\epsilon, V_\epsilon\psi_0) + (\lambda_0 - \lambda_\epsilon) + \nu_\epsilon, \end{aligned} \tag{5.20}$$

which we can re-write as

$$\lambda_\epsilon = \lambda_0 + \nu_\epsilon + (V_\epsilon\psi_0, \widehat{Y}_\epsilon). \tag{5.21}$$

Using (5.3), (5.17), and the bounds on $H_\epsilon^\perp$ from Section 5.1, we conclude that

$$\|\widehat{Y}_\epsilon\|_{L^2(\mathbb{R}^6)} \leq C\epsilon. \tag{5.22}$$

Thus (5.17), (5.21), and (5.22) combine to show that

$$|\lambda_\epsilon - \lambda_0| \leq C\epsilon^2. \tag{5.23}$$

Combining (5.19) with (5.23), we obtain

$$\|\mathcal{E}_\epsilon\|_{L^2(\mathbb{R}^6)} = \|\epsilon^{-1}\widehat{Y}_\epsilon - \psi'\|_{L^2(\mathbb{R}^6)} \leq C\epsilon^{1/3}|\log\epsilon|^3. \tag{5.24}$$

Recall that $\psi_\epsilon = \alpha_\epsilon(\widehat{Y}_\epsilon + \psi_0)$. Therefore

$$\begin{aligned} \|\psi_\epsilon - \psi_0 - \epsilon\psi'\|_{L^2(\mathbb{R}^6)} &= \|\alpha_\epsilon(\widehat{Y}_\epsilon + \psi_0) - \psi_0 - \epsilon\psi'\|_{L^2(\mathbb{R}^6)} \\ &\leq \|\widehat{Y}_\epsilon - \epsilon\psi'\|_{L^2(\mathbb{R}^6)} + |1 - \alpha_\epsilon|\,\|\widehat{Y}_\epsilon + \psi_0\|_{L^2(\mathbb{R}^6)} \\ &\leq C\epsilon^{4/3}|\log\epsilon|^3 + C|1 - \alpha_\epsilon|. \end{aligned} \tag{5.25}$$

From (5.4) and (5.22), we have

$$|1 - \alpha_\epsilon| \leq C\epsilon^2. \tag{5.26}$$

This proves the first inequality in (5.1) with $H^2(\mathbb{R}^6)$ replaced by $L^2(\mathbb{R}^6)$.

To prove the eigenvalue inequality, we return to (5.21). Thus

$$\begin{aligned} \lambda_\epsilon - \lambda_0 - \nu_\epsilon = (V_\epsilon\psi_0, \widehat{Y}_\epsilon) &= \epsilon(V_\epsilon\psi_0, \psi') + (V_\epsilon\psi_0, \widehat{Y}_\epsilon - \epsilon\psi') \\ &= \epsilon^2(\mathcal{B}\psi_0, \psi') + \epsilon((V_\epsilon - \epsilon\mathcal{B})\psi_0, \psi') + (V_\epsilon\psi_0, \widehat{Y}_\epsilon - \epsilon\psi'). \end{aligned} \tag{5.27}$$

Using (5.24) and Lemma 5.3, we find

$$|\lambda_\epsilon - \lambda_0 - \epsilon^2(\mathcal{B}\psi_0, \psi')| \leq |\nu_\epsilon| + \epsilon|((V_\epsilon - \epsilon\mathcal{B})\psi_0, \psi')| + |(V_\epsilon\psi_0, \widehat{Y}_\epsilon - \epsilon\psi')| \leq C\epsilon^{7/3}|\log\epsilon|^3. \tag{5.28}$$

This proves the second inequality in (5.1).

Now we have a lower bound on λ_ϵ, which allows us to bound $((H_\epsilon - \lambda_\epsilon)^\perp)^{-1}$ as a map from $\psi_0^\perp$ to $H^2(\mathbb{R}^6)$ as follows. Thanks to the Hardy inequality in $\mathbb{R}^3$, the quadratic form associated with the operator $H_\epsilon - \lambda_\epsilon$ is continuous and coercive, uniformly in $\epsilon \leq \epsilon_0$ on $H^1(\mathbb{R}^6) \cap \psi_0^\perp$, similar to the discussion in Section 3.3. This proves that $((H_\epsilon - \lambda_\epsilon)^\perp)^{-1}$ is a uniformly bounded map from $\psi_0^\perp$ to $H^1(\mathbb{R}^6)$. Using the Hardy inequality again, together with elliptic regularity, shows that $((H_\epsilon - \lambda_\epsilon)^\perp)^{-1}$ is a uniformly bounded map from $\psi_0^\perp$ to $H^2(\mathbb{R}^6)$. Replacing $L^2(\mathbb{R}^6)$ by $H^2(\mathbb{R}^6)$ in (5.19), (5.22), (5.24), (5.25), and (5.27) completes the proof of the first inequality in (5.1).

REMARK 5.2. *The proof Theorem 5.1 requires a type of boot-strapping with regard to estimates for λ_ϵ. The principle expressions are* (5.16) *and* (5.21)*, and they are coupled with respect to $\widehat{Y}_\epsilon$ and λ_ϵ. The first step is the simple upper bound* (5.13) *for λ_ϵ. This implies that $H_\epsilon^\perp$ is bounded on $L^2(\mathbb{R}^6)$, which in turn leads to the estimate* (5.22)*. That yields the estimate* (5.23)*, which then leads to the remaining results.*

5.4. Proof of Lemma 5.3. Estimate (5.17) follows from (3.3) by breaking the integral into two parts, one involving points at a distance no more than K from the origin, and the other integrating over the complementary domain, then choosing $K = (\log R)^4$. See [1, (3.45)] for comparison. Estimate (5.18) is proved as follows.

Recall that $R = \epsilon^{-1/3}$ and write $V_\epsilon = V_\epsilon^{(1)} + V_\epsilon^{(2)} + V_\epsilon^{(3)} + 1/2R$ following (1.6). Define the sets S_i by

$$S_i = \Big\{(\mathbf{r}_1, \mathbf{r}_2) \in \mathbb{R}^6 \,:\, |V_\epsilon^{(i)}(\mathbf{r}_1, \mathbf{r}_2)| > 1/R\Big\}. \tag{5.29}$$

Then for each $i = 1, 2, 3$, we have using (5.29) and (3.46) that

$$\|V_\epsilon^{(i)}\psi'\|_{L^2(\mathbb{R}^6)} \leq \|V_\epsilon^{(i)}\psi'\|_{L^2(S_i)} + \frac{1}{R}\|\psi'\|_{L^2(S_i^c)} \leq \|V_\epsilon^{(i)}\psi'\|_{L^2(S_i)} + \frac{C}{R}. \tag{5.30}$$

Define $B = \max\{|b(\mathbf{s}_1, \mathbf{s}_2)| \,:\, \mathbf{s}_i \in \mathbb{S}_2\}$. Then (3.28) implies, for any $q > 1$, $q' = q/(q-1)$, and $\beta \geq 0$,

$$\begin{aligned}
\|V_\epsilon^{(i)}\psi'\|_{L^2(S_i)}^2 &\leq B^2 \int_{S_i} V_\epsilon^{(i)}(\mathbf{r}_1, \mathbf{r}_2)^2 |\mathbf{r}_1|^{-2}|\mathbf{r}_2|^{-2}\, T(|\mathbf{r}_1|, |\mathbf{r}_2|)^2\, d\mathbf{r}_1 d\mathbf{r}_2 \\
&= B^2 \int_{S_i} V_\epsilon^{(i)}(\mathbf{r}_1, \mathbf{r}_2)^2 |\mathbf{r}_1|^{-2}|\mathbf{r}_2|^{-2}\, T(|\mathbf{r}_1|, |\mathbf{r}_2|)^2 e^{-(\beta/q)(|\mathbf{r}_1|+|\mathbf{r}_2|)} e^{(\beta/q)(|\mathbf{r}_1|+|\mathbf{r}_2|)}\, d\mathbf{r}_1 d\mathbf{r}_2 \\
&\leq B^2 \Big(\int_{S_i} |V_\epsilon^{(i)}(\mathbf{r}_1, \mathbf{r}_2)|^{2q} |\mathbf{r}_1|^{-2q}|\mathbf{r}_2|^{-2q}\, e^{-\beta(|\mathbf{r}_1|+|\mathbf{r}_2|)}\, d\mathbf{r}_1 d\mathbf{r}_2 \Big)^{1/q} \\
&\quad \times \Big(\int_{S_i} |T(|\mathbf{r}_1|, |\mathbf{r}_2|)|^{2q'} e^{\beta(q'/q)(|\mathbf{r}_1|+|\mathbf{r}_2|)}\, d\mathbf{r}_1 d\mathbf{r}_2 \Big)^{1/q'}.
\end{aligned} \tag{5.31}$$

But

$$\int_{S_i} |T(|\mathbf{r}_1|, |\mathbf{r}_2|)|^{2q'} e^{\beta(q'/q)(|\mathbf{r}_1|+|\mathbf{r}_2|)}\, d\mathbf{r}_1 d\mathbf{r}_2 \leq C \tag{5.32}$$

using (3.45), provided $\beta < q\sqrt{3}$. Thus it only remains to show that

$$\int_{S_i} |V_\epsilon^{(i)}(\mathbf{r}_1, \mathbf{r}_2)|^{2q} |\mathbf{r}_1|^{-2q}|\mathbf{r}_2|^{-2q}\, e^{-\beta(|\mathbf{r}_1|+|\mathbf{r}_2|)}\, d\mathbf{r}_1 d\mathbf{r}_2 \leq \frac{C}{R^{2q}} \tag{5.33}$$

for $i = 1, 2, 3$.

Case 1: Let $i = 1$. Then $S_1 = \left\{(\mathbf{r}_1, \mathbf{r}_2) \,:\, |\mathbf{r}_1 - 2R\mathbf{e}| < R,\ \mathbf{r}_2 \in \mathbb{R}^3\right\}$, $V_\epsilon^{(1)}(\mathbf{r}_1, \mathbf{r}_2) = |\mathbf{r}_1 - 2R\mathbf{e}|^{-1}$, and for $(\mathbf{r}_1, \mathbf{r}_2) \in S_1$, $|\mathbf{r}_1| \geq |2R\mathbf{e}| - |\mathbf{r}_1 - 2R\mathbf{e}| = 2R - |\mathbf{r}_1 - 2R\mathbf{e}| > R$. Thus

$$\begin{aligned}
&\int_{S_1} |V_\epsilon^{(1)}(\mathbf{r}_1, \mathbf{r}_2)|^{2q} |\mathbf{r}_1|^{-2q} |\mathbf{r}_2|^{-2q} e^{-\beta(|\mathbf{r}_1| + |\mathbf{r}_2|)}\, d\mathbf{r}_1 d\mathbf{r}_2 \\
&\quad \leq \frac{1}{R^{2q}} e^{-\beta R} \int_{S_1} |V_\epsilon^{(1)}(\mathbf{r}_1, \mathbf{r}_2)|^{2q} |\mathbf{r}_2|^{-2q} e^{-\beta|\mathbf{r}_2|}\, d\mathbf{r}_1 d\mathbf{r}_2 \\
&\quad = \frac{1}{R^{2q}} e^{-\beta R} \int_{\mathbb{R}^3} \left(\int_{|\mathbf{r}_1 - 2R\mathbf{e}| \leq R} |\mathbf{r}_1 - 2R\mathbf{e}|^{-2q}\, d\mathbf{r}_1 \right) |\mathbf{r}_2|^{-2q} e^{-\beta|\mathbf{r}_2|}\, d\mathbf{r}_2 \leq \frac{C_q}{R^{4q-3}} e^{-\beta R}
\end{aligned} \tag{5.34}$$

provided $q < 3/2$. Choosing e.g. $q = 10/7$ and $\beta = 1/3$ yields (5.33).

Case 2: By reversing the roles of $\mathbf{r}_1$ and $\mathbf{r}_2$, we prove (5.33) for $i = 2$ under the same conditions.

Case 3: We have $S_3 = \left\{(\mathbf{r}_1, \mathbf{r}_2) \,:\, |\mathbf{r}_1 - \mathbf{r}_2 - 2R\mathbf{e}| < R,\ \mathbf{r}_2 \in \mathbb{R}^3\right\}$. For $|\mathbf{r}_1 - \mathbf{r}_2 - 2R\mathbf{e}| \leq R$,

$$2R = |2R\mathbf{e}| \leq |\mathbf{r}_1 - \mathbf{r}_2 - 2R\mathbf{e}| + |\mathbf{r}_1 - \mathbf{r}_2| \leq R + |\mathbf{r}_1 - \mathbf{r}_2| \leq R + |\mathbf{r}_1| + |\mathbf{r}_2|,$$

so that

$$R \leq |\mathbf{r}_1| + |\mathbf{r}_2| \leq \sqrt{2(|\mathbf{r}_1|^2 + |\mathbf{r}_2|^2)} \ \text{ for } (\mathbf{r}_1, \mathbf{r}_2) \in S_3. \tag{5.35}$$

But (5.35) implies that for $(\mathbf{r}_1, \mathbf{r}_2) \in S_3$, either $|\mathbf{r}_1| \geq \frac{1}{2}R$ or $|\mathbf{r}_2| \geq \frac{1}{2}R$. Define

$$S_3^1 = \left\{(\mathbf{r}_1, \mathbf{r}_2) \in S_3 \,:\, |\mathbf{r}_1| \geq \tfrac{1}{2}R\right\} \ \text{ and } \ S_3^2 = \left\{(\mathbf{r}_1, \mathbf{r}_2) \in S_3 \,:\, |\mathbf{r}_2| \geq \tfrac{1}{2}R\right\}. \tag{5.36}$$

Then $S_3 \subset S_3^1 \cup S_3^2$. On S_3^1, we get

$$\begin{aligned}
&\int_{S_3^1} |V_\epsilon^{(3)}(\mathbf{r}_1, \mathbf{r}_2)|^{2q} |\mathbf{r}_1|^{-2q} |\mathbf{r}_2|^{-2q} e^{-\beta(|\mathbf{r}_1| + |\mathbf{r}_2|)}\, d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \int_{S_3^1} |\mathbf{r}_1 - \mathbf{r}_2 - 2R\mathbf{e}|^{-2q} |\mathbf{r}_1|^{-2q} |\mathbf{r}_2|^{-2q} e^{-\beta(|\mathbf{r}_1| + |\mathbf{r}_2|)}\, d\mathbf{r}_1 d\mathbf{r}_2 \\
&\leq \frac{2^{2q}}{R^{2q}} e^{-\beta R/2} \int_{S_3^1} |\mathbf{r}_1 - \mathbf{r}_2 - 2R\mathbf{e}|^{-2q} |\mathbf{r}_2|^{-2q} e^{-\beta|\mathbf{r}_2|}\, d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \frac{2^{2q}}{R^{2q}} e^{-\beta R/2} \int_{\mathbb{R}^3} \Big(\int_{|\mathbf{r}_1 - \mathbf{r}_2 - 2R\mathbf{e}| \leq R} |\mathbf{r}_1 - \mathbf{r}_2 - 2R\mathbf{e}|^{-2q}\, d\mathbf{r}_1 \Big) |\mathbf{r}_2|^{-2q} e^{-\beta|\mathbf{r}_2|}\, d\mathbf{r}_2 \leq \frac{C_q'}{R^{4q-3}} e^{-\beta R/2},
\end{aligned} \tag{5.37}$$

provided $q < 3/2$.

Reversing the roles of $\mathbf{r}_1$ and $\mathbf{r}_2$ proves that a similar result holds for the integral over S_3^2, so choosing again $q = 10/7$ and $\beta = 1$ yields (5.33).

6. Further comments. The limiting expression (2.2) for the energy difference for hydrogen-hydrogen interaction is accurate for separation distances greater than 10 Bohr (about 5 Ångstroms), but it deviates dramatically from this model for smaller separation distances, as shown in Figure 3.1. One attempt [2] to explain this discrepancy involves the term $\nu_\epsilon = (\psi_0, V_\epsilon \psi_0)$ in (2.14). But this contribution is no larger than $C_6 R^{-6}$ in magnitude, exceeding it only slightly for R near 3.86 Bohr. Thus ν_ϵ is about an order of magnitude too small to explain the discrepancy in Figure 3.1 in the range, say, of 6 to 10 Bohr (3 to 5 Ångstroms). Adding the C_8 and C_{10} terms in [4] similarly fails to account for the rapid change in energy in the range $R \in [5, 10]$. Perturbation theory is therefore not an appropriate tool to compute the H–H interaction energy in this separation range, in which it is necessary to solve the full 6D Schrödinger equation or one of its approximations (MCSCF, coupled cluster, ...) [9].

It is known [4] that C_7 and C_9 are both zero. To prove such a result would require more terms in the approximation of V_ϵ, cf. (3.3).

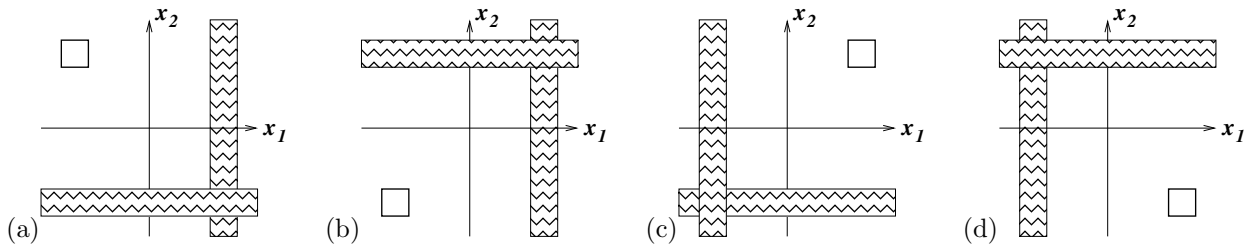

FIG. A.1. *Hashed areas indicate locations of the negative singularities of the interaction potentials for two decompositions. The open squares indicate the presumed location of the electrons. In (a), the assumption is that the i-th electron is near the i-th proton; the hashed areas depict* $(\Omega_R^1)^c$. *In (b), both electrons are assumed to be close to just one proton (the ionic case); the hashed areas depict* $(\Omega_R^2)^c$. *In (c), both electrons are assumed to be close to just one proton (the other ionic case); the hashed areas depict* $(\Omega_R^2)^c$. *In (d), the assumption is that the i-th electron is near the j-th proton, where* $\{i,j\} = \{1,2\}$*; the hashed areas depict* $(\Omega_R^3)^c$.

Lastly, it is worth emphasizing that the Schrödinger equations are only a model of physics, not physical reality. In particular, for modeling van der Waals interactions, there is a different model with different properties. The Casimir-Polder model [3] involves quantum electrodynamics and obtains an interaction energy that decays like $\mathcal{O}\left(R^{-7}\right)$. According to [11], the latter model becomes significant at a distance of 100 Bohr, or about 53 Ångstroms.

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Appendix A. Proof of Lemma 5.2.

The following proof is a specialization of the proof in [1] to the hydrogen molecule, and it is included for completeness. Comparing (5.7) with (5.12), we see that, to prove Lemma 5.2, we have to show that V_ϵ can be viewed as a small perturbation. The latter would seem to be a result of (5.17), but the difficulty is that there are (negative) singularities in V_ϵ, as indicated by the hashed regions in Figure A.1(a). These singularities occur at distant places, but nevertheless we need to deal with them. We will do so by looking at different decompositions of H_ϵ in which the corresponding singularities appear at different places [1].

A.1. The ionic view point. The decomposition of the Schrödinger equation given in (1.4) suggests a prejudice that the electron associated with position $\mathbf{r}_i$ is close to the proton at $(-1)^i \frac{1}{2} R\mathbf{e}$. But we can take a different point of view in which we write the Schrödinger operator as

$$H_\epsilon = -\tfrac{1}{2}\Delta_{\mathbf{r}_1} - \tfrac{1}{2}\Delta_{\mathbf{r}_2} - \frac{1}{|\mathbf{r}_1 + \frac{1}{2}R\mathbf{e}|} - \frac{1}{|\mathbf{r}_2 + \frac{1}{2}R\mathbf{e}|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + V_\epsilon^1 = H^- + V_\epsilon^1, \tag{A.1}$$

where the correlation potential V_ϵ^1 satisfies

$$V_\epsilon^1(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{|\mathbf{r}_1 - \frac{1}{2}R\mathbf{e}|} - \frac{1}{|\mathbf{r}_2 - \frac{1}{2}R\mathbf{e}|} + \frac{1}{R}, \tag{A.2}$$

and H^- is defined in (5.8). The singularities in the interaction potential V_ϵ^1 are in different places. More precisely, the hashed areas of Figure A.1(b) represent the complement $(\Omega_R^1)^c$ of the set of points

$$\Omega_R^1 = \left\{(\mathbf{r}_1, \mathbf{r}_2) \,:\, \mathbf{r}_i \in \mathbb{R}^3,\ |\mathbf{r}_1 - \tfrac{1}{2}R\mathbf{e}| > \beta R \text{ and } |\mathbf{r}_2 - \tfrac{1}{2}R\mathbf{e}| > \beta R\right\}, \tag{A.3}$$

where β will be fixed in the interval $0 < \beta < 1$. On the set Ω_R^1 we can guarantee that $V_\epsilon^1 \geq -2/\beta R$.

The tacit thinking in the decomposition (A.1) is that the electrons are located near the proton at $-\frac{1}{2}R\mathbf{e}$, mostly inside the open box B_R^1 indicated in Figure A.1(b), defined by

$$B_R^1 = \left\{(\mathbf{r}_1, \mathbf{r}_2) \,:\, \mathbf{r}_i \in \mathbb{R}^3,\ |\mathbf{r}_1 + \tfrac{1}{2}R\mathbf{e}| \leq \beta R \text{ and } |\mathbf{r}_2 + \tfrac{1}{2}R\mathbf{e}| \leq \beta R\right\}. \tag{A.4}$$

Correspondingly, the hashed areas in Figure A.1(a) depict the complement of the set

$$\Omega_R^0 = \left\{(\mathbf{r}_1, \mathbf{r}_2) \,:\, \mathbf{r}_i \in \mathbb{R}^3,\ |\mathbf{r}_1 - \tfrac{1}{2}R\mathbf{e}| > \beta R \text{ and } |\mathbf{r}_2 + \tfrac{1}{2}R\mathbf{e}| > \beta R\right\}, \tag{A.5}$$

and on Ω_R^0 we can guarantee that $V_\epsilon \geq -2/\beta R$. The tacit thinking in the decomposition (1.4) is that the i-th electron is located near the proton at $(-1)^i \frac{1}{2}R\mathbf{e}$, mostly inside the open box B_R^0 indicated in Figure A.1(a), defined by

$$B_R^0 = \left\{(\mathbf{r}_1, \mathbf{r}_2) \,:\, \mathbf{r}_i \in \mathbb{R}^3,\ |\mathbf{r}_1 + \tfrac{1}{2}R\mathbf{e}| \leq \beta R \text{ and } |\mathbf{r}_2 - \tfrac{1}{2}R\mathbf{e}| \leq \beta R\right\}. \tag{A.6}$$

We can equally assume that that the electrons are near the other proton, giving the decomposition

$$H_\epsilon = -\tfrac{1}{2}\Delta_{\mathbf{r}_1} - \tfrac{1}{2}\Delta_{\mathbf{r}_2} - \frac{1}{|\mathbf{r}_1 - \frac{1}{2}R\mathbf{e}|} - \frac{1}{|\mathbf{r}_2 - \frac{1}{2}R\mathbf{e}|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + V_\epsilon^2 = H^- + V_\epsilon^2, \tag{A.7}$$

where the correlation potential V_ϵ^2 satisfies

$$V_\epsilon^2(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{|\mathbf{r}_1 + \frac{1}{2}R\mathbf{e}|} - \frac{1}{|\mathbf{r}_2 + \frac{1}{2}R\mathbf{e}|} + \frac{1}{R} \tag{A.8}$$

and H^- is defined in (5.8). The locations of negative singularites of V_ϵ^2 are depicted in Figure A.1(c).

There remains a common point of negative singularity between the potentials V_ϵ, V_ϵ^1, and V_ϵ^2, near the point $\mathbf{r}_1 = \mathbf{r}_2 = \frac{1}{2}R\mathbf{e}$. However, if we simply reverse the ordering of the electrons in the original decomposition (1.4), we obtain the decomposition

$$H_\epsilon = -\tfrac{1}{2}\Delta_{\mathbf{r}_1} - \tfrac{1}{2}\Delta_{\mathbf{r}_2} - \frac{1}{|\mathbf{r}_1 - \frac{1}{2}R\mathbf{e}|} - \frac{1}{|\mathbf{r}_2 + \frac{1}{2}R\mathbf{e}|} + V_\epsilon^3, \tag{A.9}$$

where the correlation potential V_ϵ^3 satisfies

$$V_\epsilon^3(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{|\mathbf{r}_1 + \frac{1}{2}R\mathbf{e}|} - \frac{1}{|\mathbf{r}_2 - \frac{1}{2}R\mathbf{e}|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{R}, \tag{A.10}$$

(recall $\mathbf{e} = (1, 0, 0)$), and we assume that proton i is located at $(-1)^i \frac{1}{2}R\mathbf{e}$. This corresponds to the Hamiltonian for the original hydrogen pair, just with the labels re-ordered.

In Figure A.1(c-d), we have plotted the complements of the sets of points

$$\begin{aligned}
\Omega_R^2 &= \left\{(\mathbf{r}_1, \mathbf{r}_2) \,:\, \mathbf{r}_i \in \mathbb{R}^3,\ |\mathbf{r}_1 + \tfrac{1}{2}R\mathbf{e}| > \beta R \text{ and } |\mathbf{r}_2 + \tfrac{1}{2}R\mathbf{e}| > \beta R\right\}, \\
\Omega_R^3 &= \left\{(\mathbf{r}_1, \mathbf{r}_2) \,:\, \mathbf{r}_i \in \mathbb{R}^3,\ |\mathbf{r}_1 + \tfrac{1}{2}R\mathbf{e}| > \beta R \text{ and } |\mathbf{r}_2 - \tfrac{1}{2}R\mathbf{e}| > \beta R\right\}.
\end{aligned} \tag{A.11}$$

together with the open boxes

$$\begin{aligned}
B_R^2 &= \left\{(\mathbf{r}_1, \mathbf{r}_2) \,:\, \mathbf{r}_i \in \mathbb{R}^3,\ |\mathbf{r}_1 - \tfrac{1}{2}R\mathbf{e}| \leq \beta R \text{ and } |\mathbf{r}_2 - \tfrac{1}{2}R\mathbf{e}| \leq \beta R\right\} \\
B_R^3 &= \left\{(\mathbf{r}_1, \mathbf{r}_2) \,:\, \mathbf{r}_i \in \mathbb{R}^3,\ |\mathbf{r}_1 - \tfrac{1}{2}R\mathbf{e}| \leq \beta R \text{ and } |\mathbf{r}_2 + \tfrac{1}{2}R\mathbf{e}| \leq \beta R\right\}.
\end{aligned} \tag{A.12}$$

To unify notation, we denote by V_ϵ^0 the original potential in (1.6). With these definitions, we have $H_\epsilon = H_\epsilon^i + V_\epsilon^i$ with

$$V_\epsilon^i(\mathbf{r}_1, \mathbf{r}_2) \geq -2/\beta R \quad \forall (\mathbf{r}_1, \mathbf{r}_2) \in \Omega_R^i, \tag{A.13}$$

for $i = 0, 1, 2, 3$. Furthermore, $H_\epsilon^i \geq \lambda_0 + \gamma_0$ for $i = 1, 2$ and $P^\perp H_\epsilon^i P^\perp \geq \lambda_0 + \gamma_0$ for $i = 0, 3$.

A.2. General decompositions. In [1], general decompositions are considered that associate electrons with protons. Let us denote the four ordered decompositions of $\{1,2\}$ considered so far by $a_i = [A_1, A_2]$ with $i = 0,1,2,3$, given by the definitions

$$a_0 = [\{1\},\{2\}], \quad a_1 = [\{1,2\},\emptyset], \quad a_2 = [\emptyset,\{1,2\}], \quad a_3 = [\{2\},\{1\}]. \tag{A.14}$$

Note that in all cases we have $a_i = [A_1, A_2]$ with $A_1 \cup A_2 = \{1,2\}$ and $A_1 \cap A_2 = \emptyset$. Thus each decomposition a_i of electrons corresponds to a different interaction potential V_ϵ^i having different postions for the negative singularities. More precisely, we have

$$\bigcap_{i=0}^{3} (\Omega_R^i)^c = \emptyset. \tag{A.15}$$

Therefore the open sets Ω_R^i form an open covering of $\mathbb{R}^3$. So we can pick [1] a subordinate partition of unity J_i (that is, the closure of the support of J_i is contained in Ω_R^i for all i) with the properties that $\sum_{i=0}^3 J_i^2 = 1$, together with $0 \le J_i(\mathbf{r}) \le 1$ for all $\mathbf{r} \in \mathbb{R}^3$, and $\|D^\alpha J_i\|_{L^\infty(\mathbb{R}^3)} \le C_{|\alpha|}(\beta R)^{-|\alpha|}$, where β is the constant in the definitions of Ω_R^i and B_R^i. Moreover, $J_i(\mathbf{r})^2 V_\epsilon^i(\mathbf{r}) \ge -2/(\beta R)\ \forall \mathbf{r} \in \mathbb{R}^3$, in view of (A.13), since $J_i(\mathbf{r}) = 0$ for $\mathbf{r} \notin \Omega_R^i$. Notice that for any $i = 0,1,2,3$, if we define $\ell_i = \{j = 0,1,2,3 : j \ne i\}$, then $\bigcap_{j\in\ell_i} (\Omega_R^j)^c = B_R^i$. Thus we conclude that $J_i \equiv 1$ on B_R^i for all $i = 0,1,2,3$.

Now we use the IMS localization formula [6, page 28] to write $H_\epsilon = \sum_{i=0}^3 J_i H_\epsilon J_i - |\nabla J_i|^2$. Therefore

$$\begin{aligned} H_\epsilon &= \sum_{i=0}^{3} J_i H_\epsilon J_i - |\nabla J_i|^2 = \sum_{i=0}^{3} J_i H_\epsilon^i J_i + J_i V_\epsilon^i J_i - |\nabla J_i|^2 \\ &\ge \sum_{i=0}^{3} J_i H_\epsilon^i J_i + J_i V_\epsilon^i J_i - \frac{C}{(\beta R)^2} \ge \sum_{i=0}^{3} J_i H_\epsilon^i J_i - \frac{2}{\beta R} - \frac{C}{(\beta R)^2}. \end{aligned} \tag{A.16}$$

Since $H_\epsilon^i \ge \lambda_0 + \gamma_0$ for $i = 1,2$, we have

$$P^\perp J_i H_\epsilon^i J_i P^\perp \ge (\lambda_0 + \gamma_0) P^\perp J_i^2 P^\perp \tag{A.17}$$

for $i = 1,2$. Similarly $P^\perp H_\epsilon^i P^\perp \ge \lambda_0 + \gamma_0$ for $i = 0,3$ and thus $J_i P^\perp H_\epsilon^i P^\perp J_i \ge (\lambda_0 + \gamma_0) J_i P^\perp J_i$ for $i = 0,3$. We can then obtain (A.17) for $i = 0,3$ from the following:

$$P^\perp J_i H_\epsilon^i J_i P^\perp \ge J_i P^\perp H_\epsilon^i P^\perp J_i - C e^{-\beta R}, \quad \text{for } i = 0,3. \tag{A.18}$$

This allows us to conclude that

$$P^\perp J_i H_\epsilon^i J_i P^\perp \ge (\lambda_0 + \gamma_0) J_i P^\perp J_i - C e^{-\beta R} \tag{A.19}$$

for $i = 0,3$ (compare this with (A.17)). The proof of (A.18) is straightforward, although lengthy [1].

To complete the proof of Lemma 5.2, we need to bound $J_i P^\perp J_i$ (see (A.19)) in terms of $P^\perp J_i^2 P^\perp$ (see (A.17)). Again, straightforward arguments [1] yield

$$J_i P^\perp J_i - P^\perp J_i^2 P^\perp \ge -C e^{-\beta R}. \tag{A.20}$$

Thus we have proved that

$$P^\perp J_i H_\epsilon^i J_i P^\perp \ge (\lambda_0 + \gamma_0) P^\perp J_i^2 P^\perp - C e^{-\beta R}, \tag{A.21}$$

for $i = 0,1,2,3$. Applying (A.16), we conclude that

$$H_\epsilon^\perp \ge (\lambda_0 + \gamma_0) - \frac{2}{\beta R} - \frac{C}{(\beta R)^2} - C e^{-\beta R}, \tag{A.22}$$

and this completes the proof of Lemma 5.2.

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